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(52) UK CL (Edition S)

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F302 F307 F802  
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Vol. 51, No. 15, 12 October 1987, pa s 1143-1145

(58) continued overleaf

(54) Abstract Title

Atomic layer deposition method

(57) In a method of forming a thin film using an atomic layer deposition (ALD) method, a thin film is formed on a substrate in a cycle of injecting a first reactant including an atom that forms the thin film and a ligand into a reaction chamber that includes the substrate, purging the first reactant, injecting a second reactant into the reaction chamber, and purging the second reactant. The thin film is formed by a chemical reaction between the atom that forms the thin film and a second reactant whose binding energy with respect to the atom that forms the thin film is larger than the binding energy of the ligand with respect to the atom that forms the thin film and the generation of by-products is prevented. The generation of a hydroxide by-product in the thin film is suppressed by using a material that does not include a hydroxide as the second reactant, purging the second reactant, and reacting the second reactant with a third reactant that includes hydroxide. After purging the second reactant, the third reactant for removing impurities and improving the stoichiometry of the thin film is injected and purged. By doing so, it is possible to obtain a thin film, which does not include impurities and whose stoichiometry is excellent. The dangling bond of the surface of the substrate is terminated by injecting oxidising gas before injecting the first reactant is  $\text{Al}(\text{CH}_3)_3$  the second reactant is  $\text{O}_3$ ,  $\text{O}_2$ , or  $\text{N}_2\text{O}$ . When the first reactant is a metal, the second reactant is  $\text{N}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{O}_3$ , or  $\text{CO}_2$ , and the third reactant is an oxidising gas.

FIG. 3

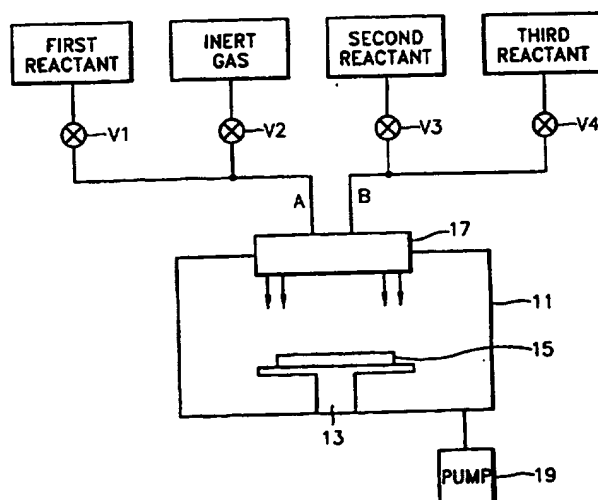
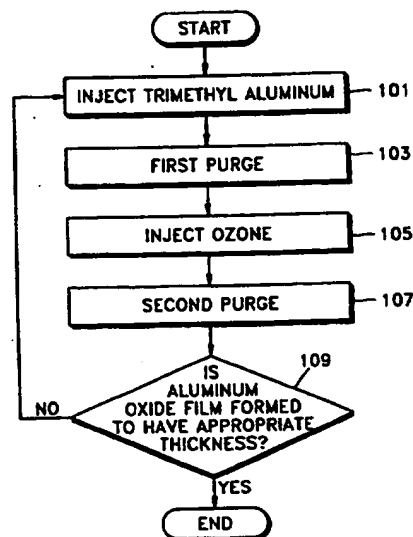


FIG. 5



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Sung-je Choi  
Sang-in Lee  
Jae-soon Lim**

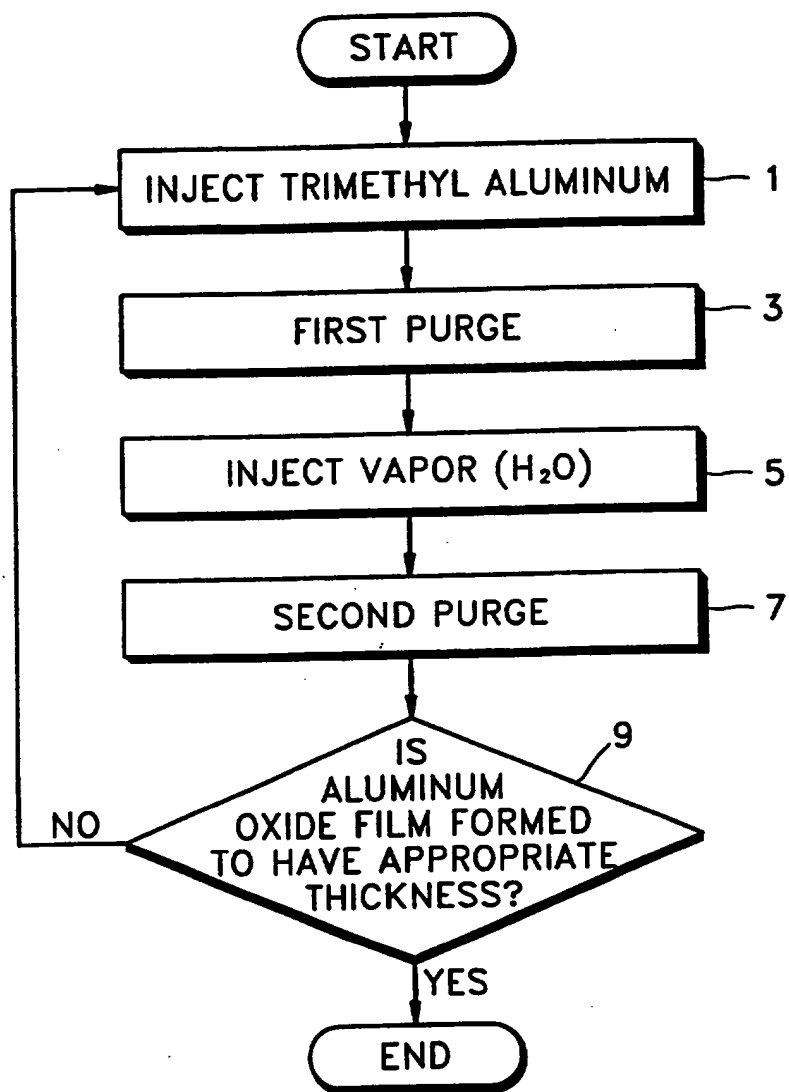
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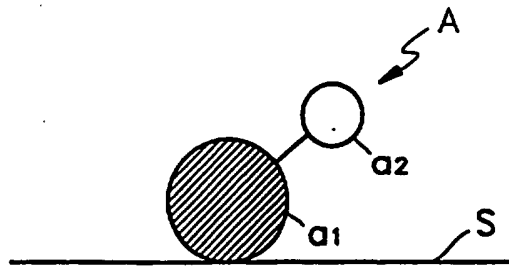
**(58) Field of Search**

**UK CL (Edition S ) C7F FCVE FCVL FCVM FCVX FCXE  
FCXL FCXM FCXX FHB FHE FHX  
INT CL<sup>7</sup> C23C 14/00 14/08 16/44 , C30B 23/02 23/08 25/00  
25/02 , H01L 21/316  
Online: WPI, EPODOC, JAPIO**

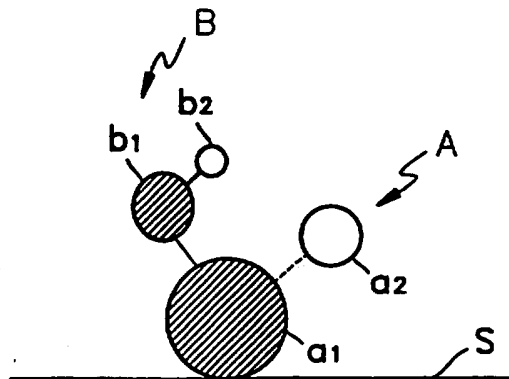
FIG. 1  
(PRIOR ART)



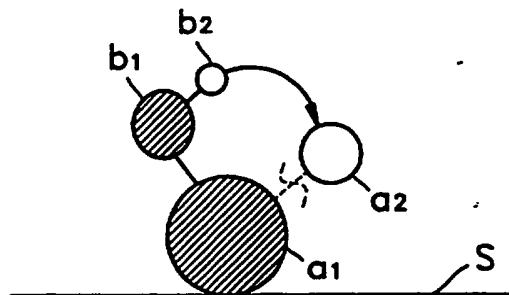
**FIG. 2A**  
(PRIOR ART)



**FIG. 2B**  
(PRIOR ART)



**FIG. 2C**  
(PRIOR ART)



**FIG. 2D**  
(PRIOR ART)

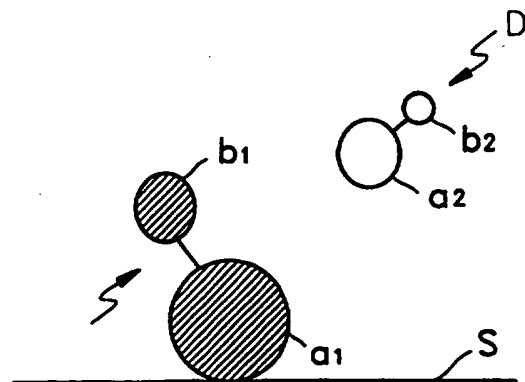


FIG. 3

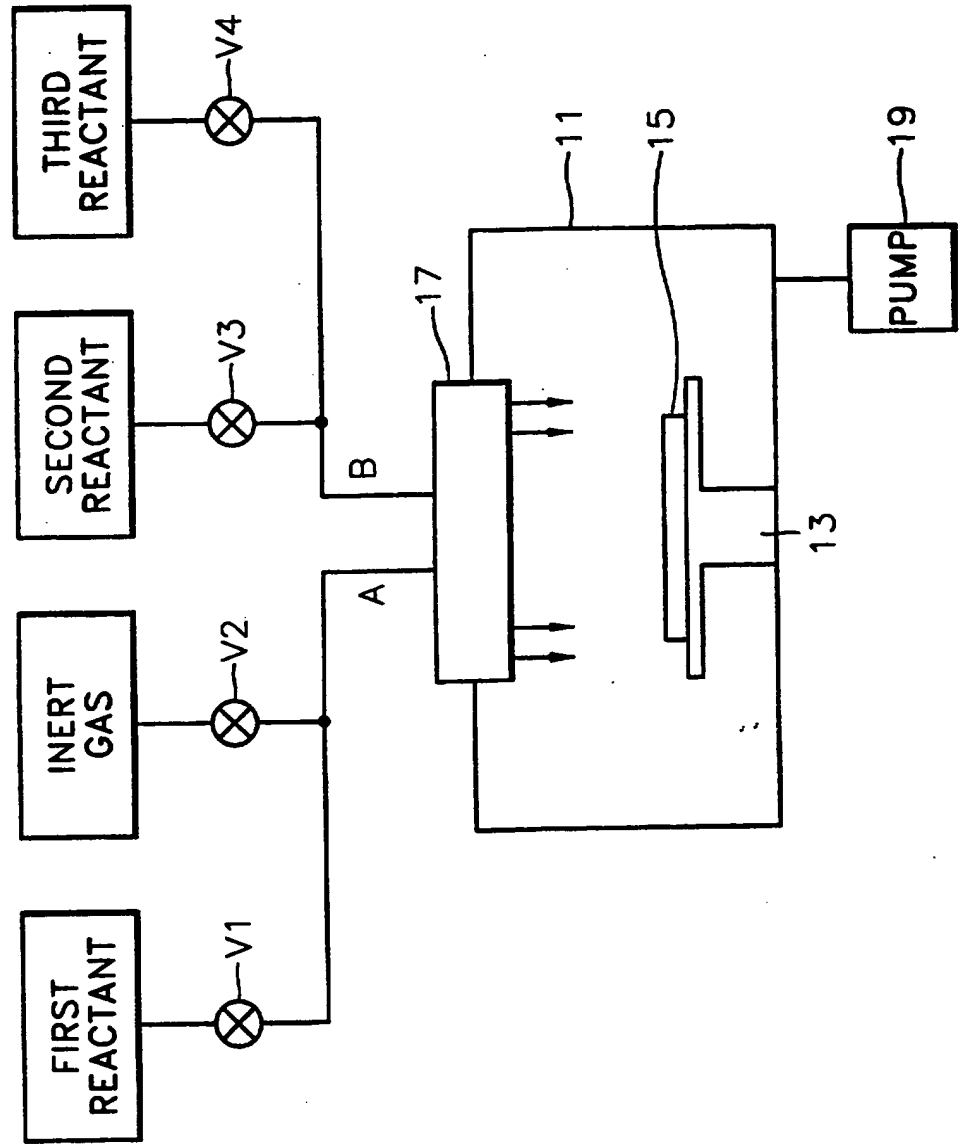


FIG. 4A

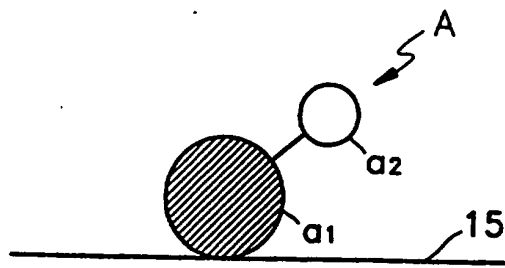


FIG. 4B

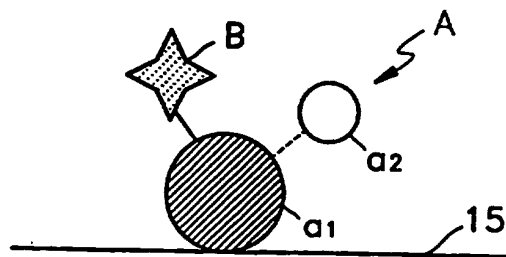


FIG. 4C

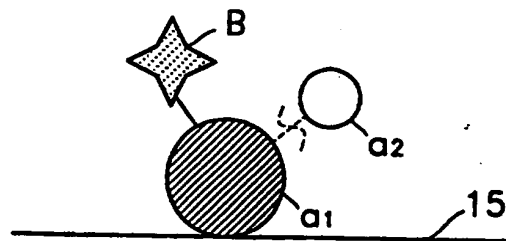


FIG. 4D

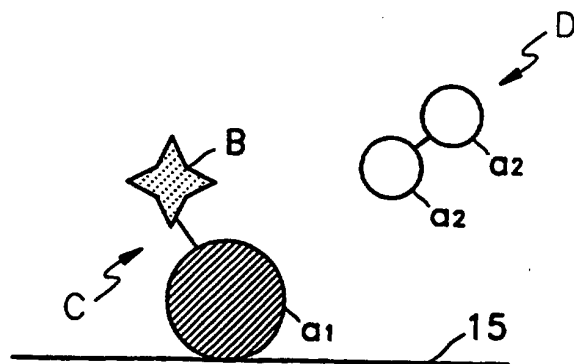


FIG. 5

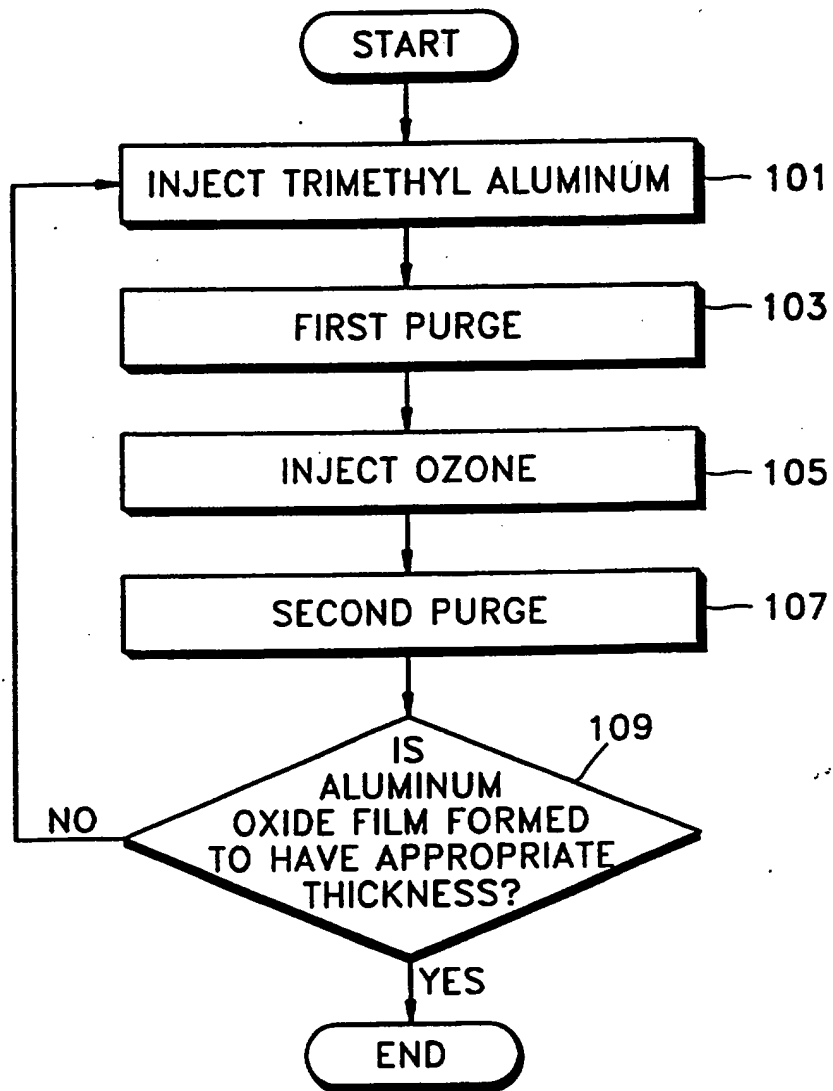


FIG. 6A

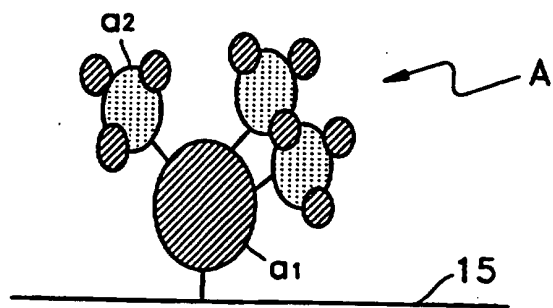


FIG. 6B

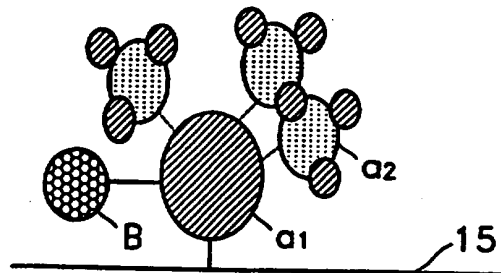


FIG. 6C

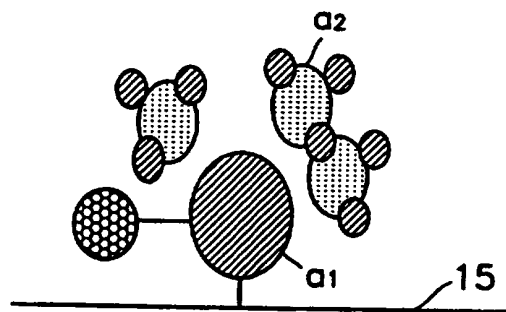
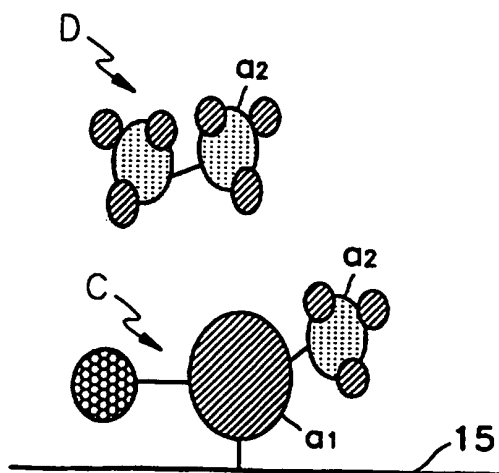


FIG. 6D





1127  
FIG. 7

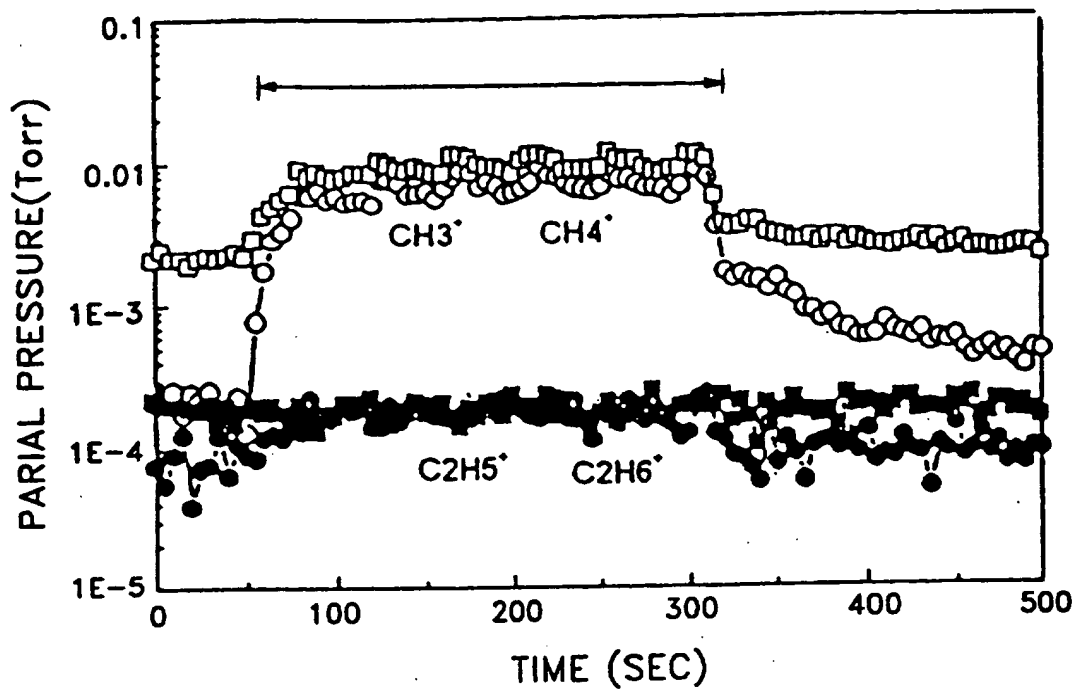
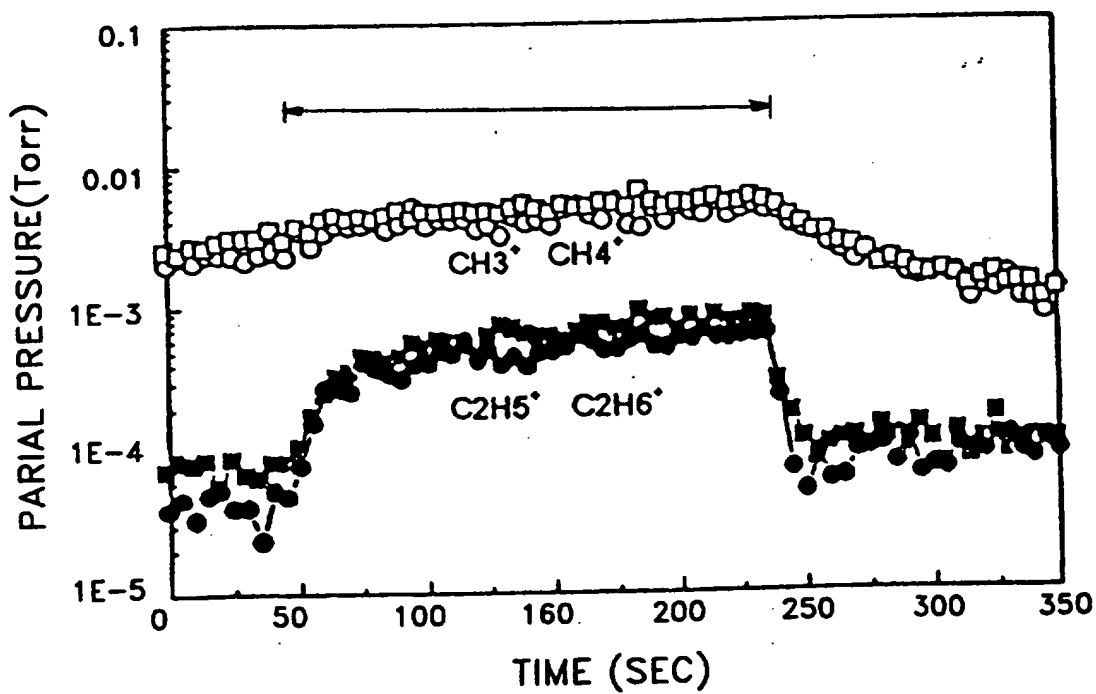


FIG. 8



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FIG. 9

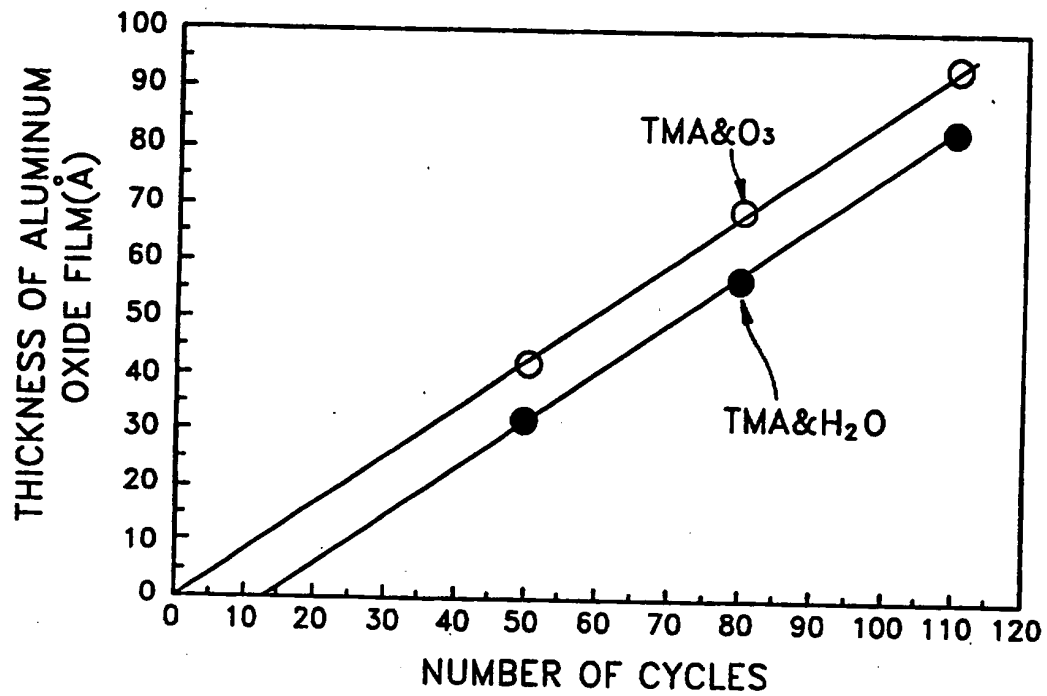


FIG. 10

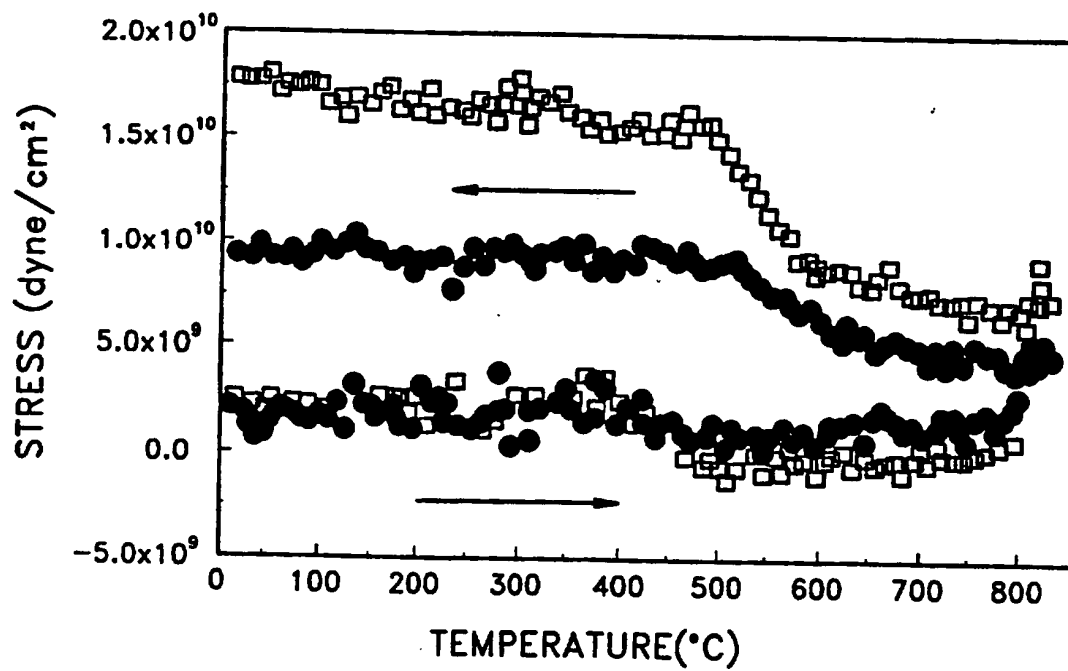


FIG. 11

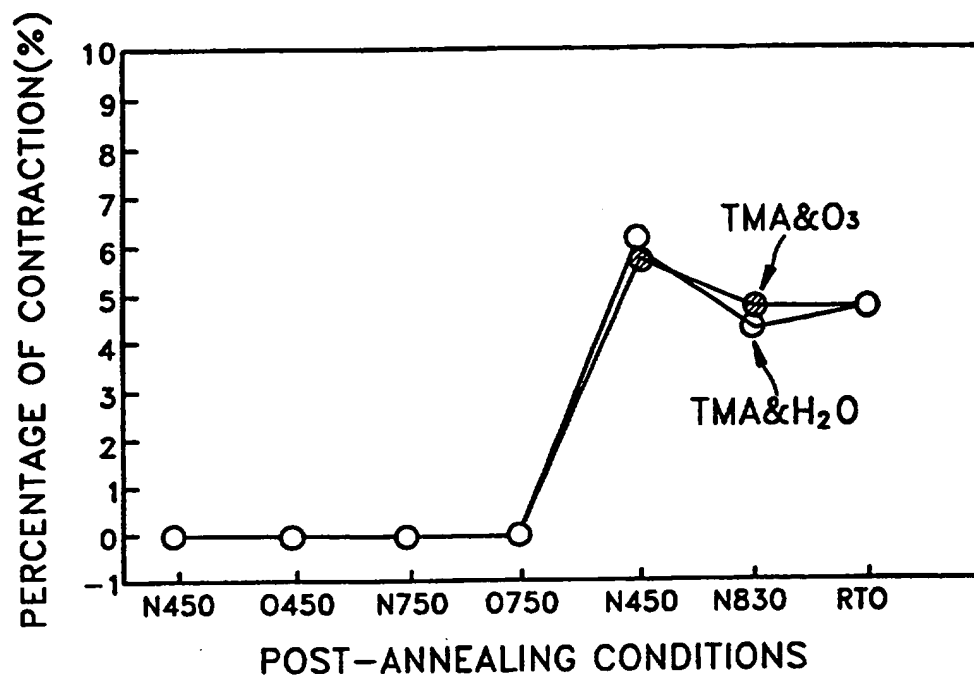


FIG. 12

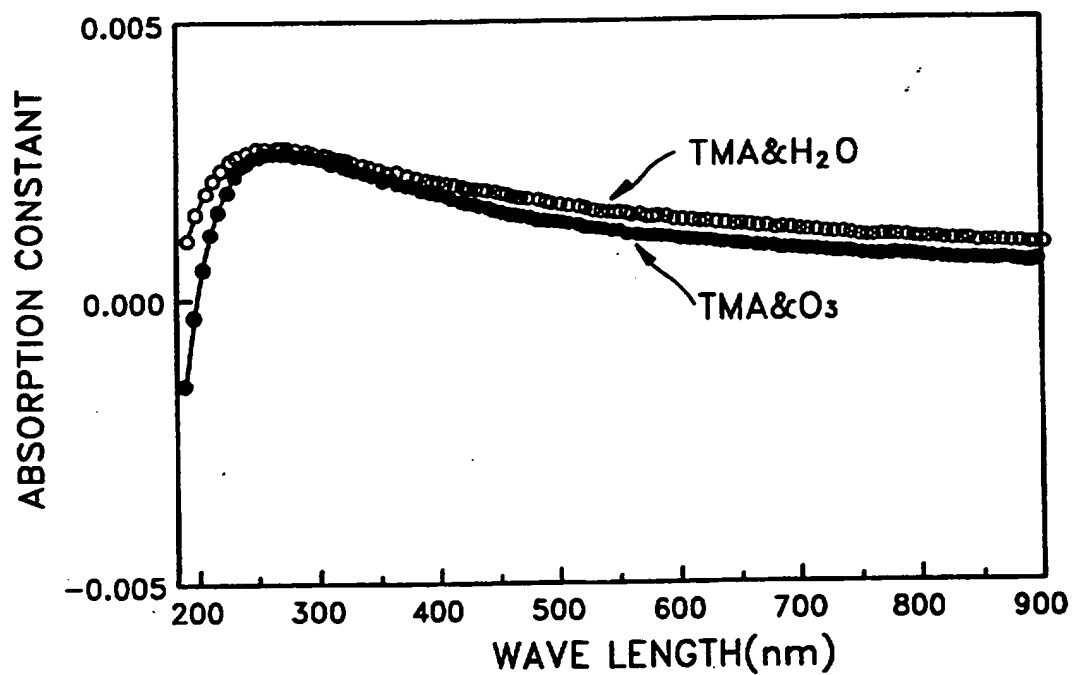


FIG. 13

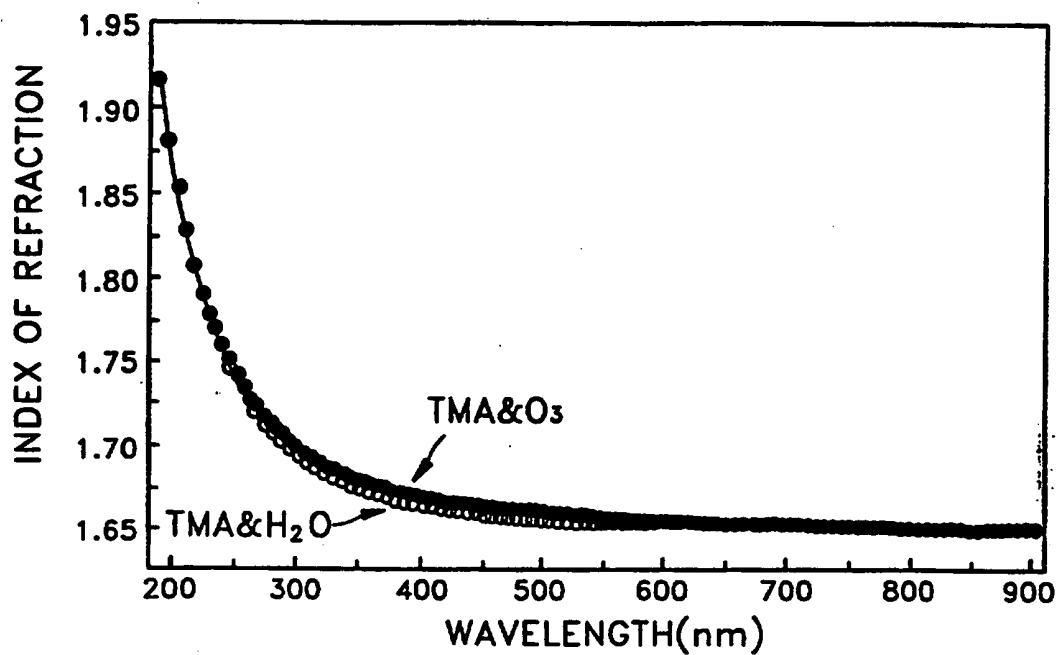


FIG. 14

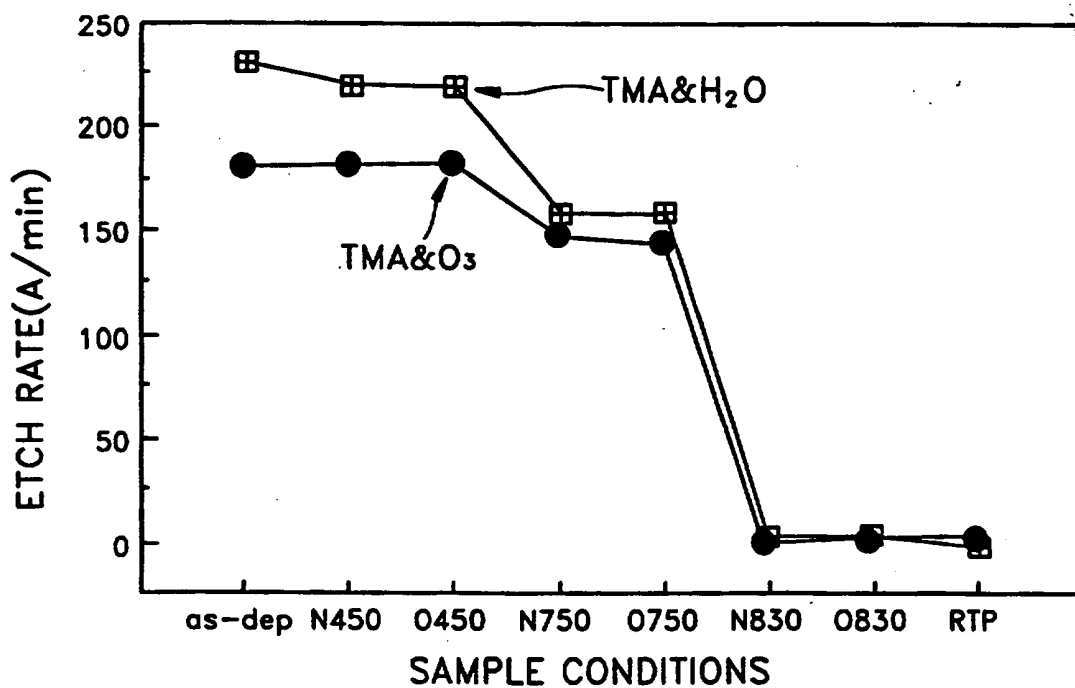


FIG. 15

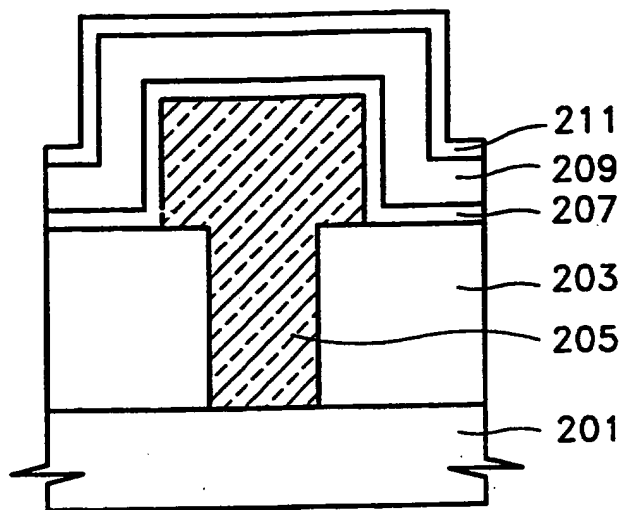
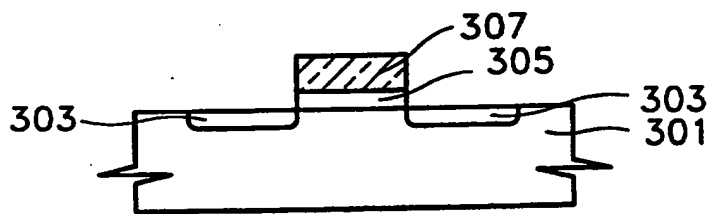


FIG. 16



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FIG. 17

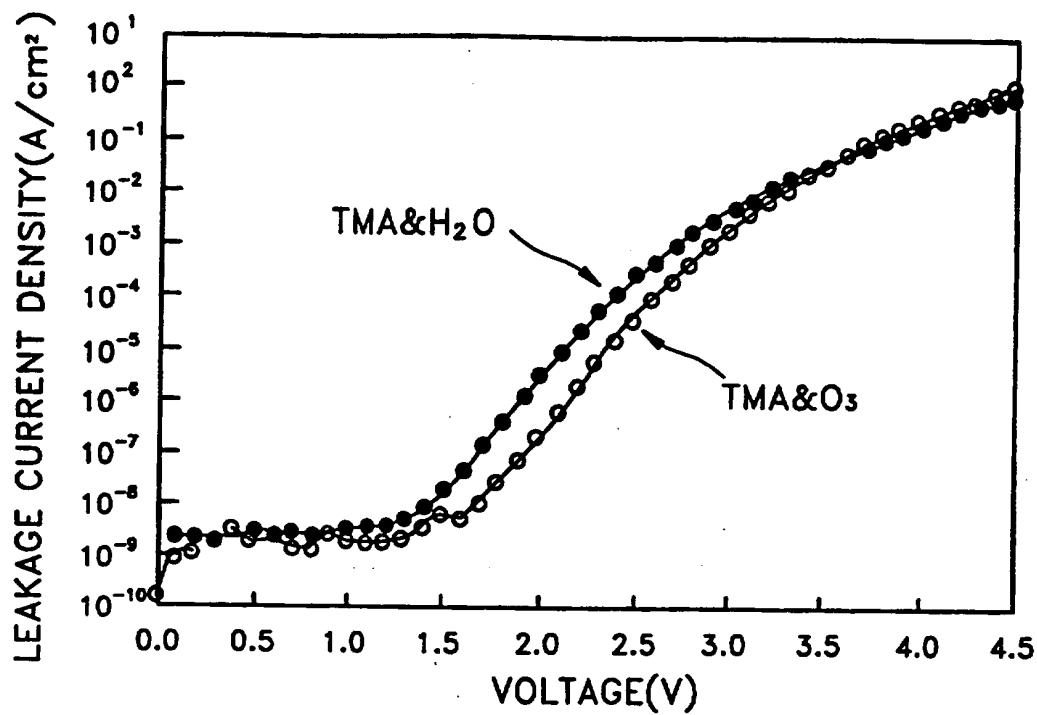
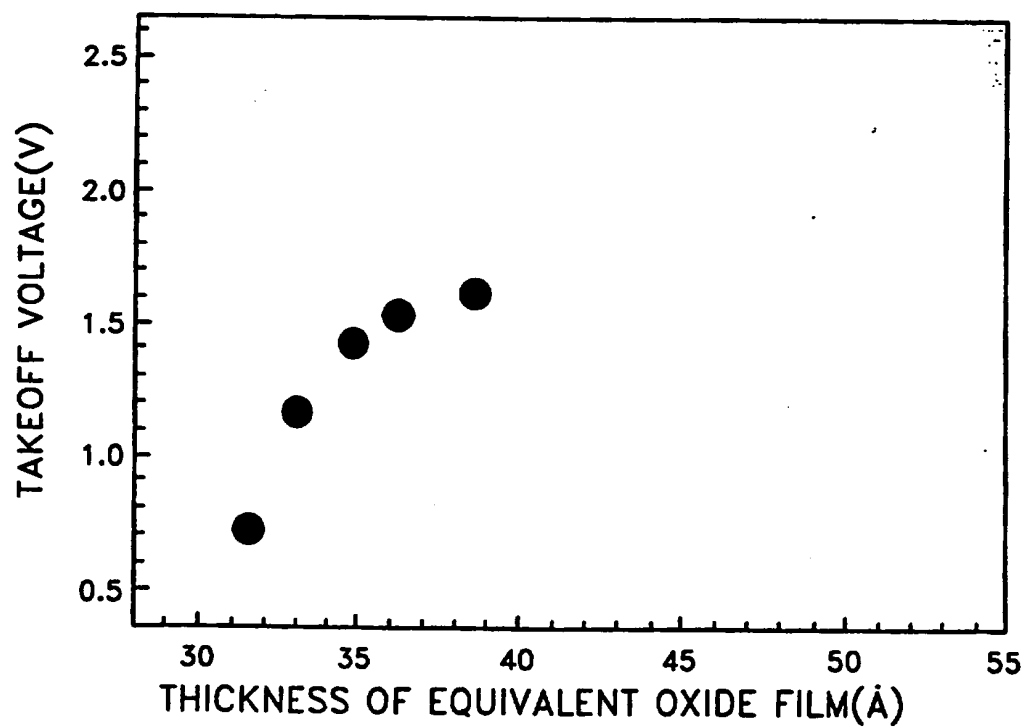


FIG. 18



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FIG. 19

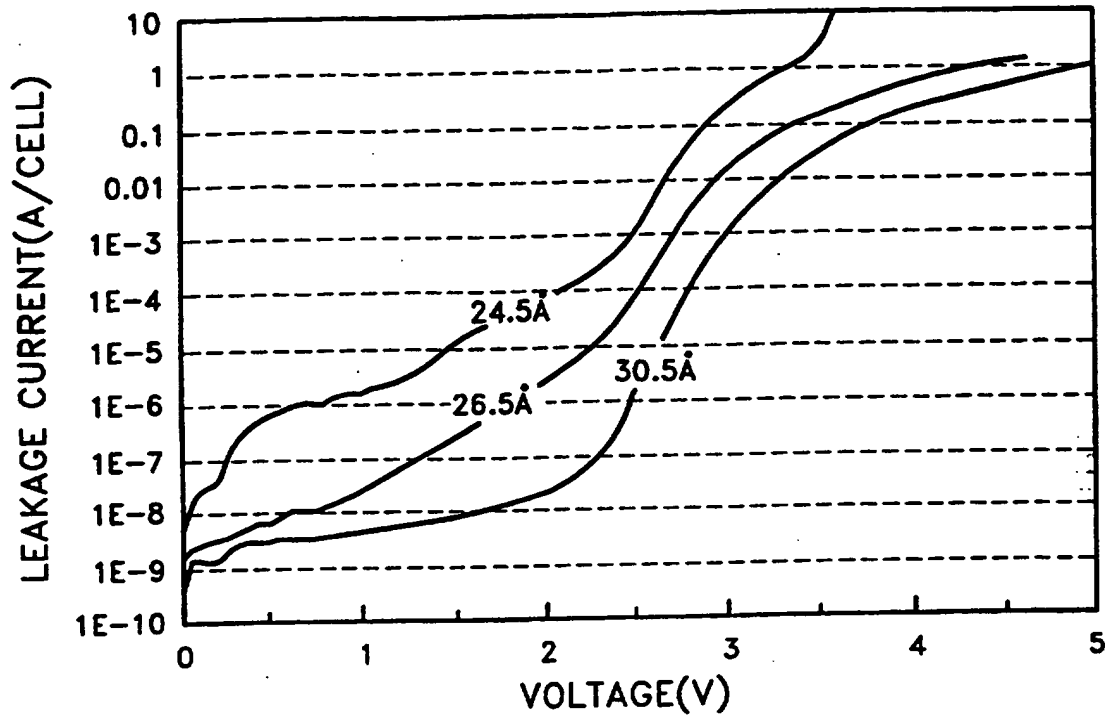


FIG. 20

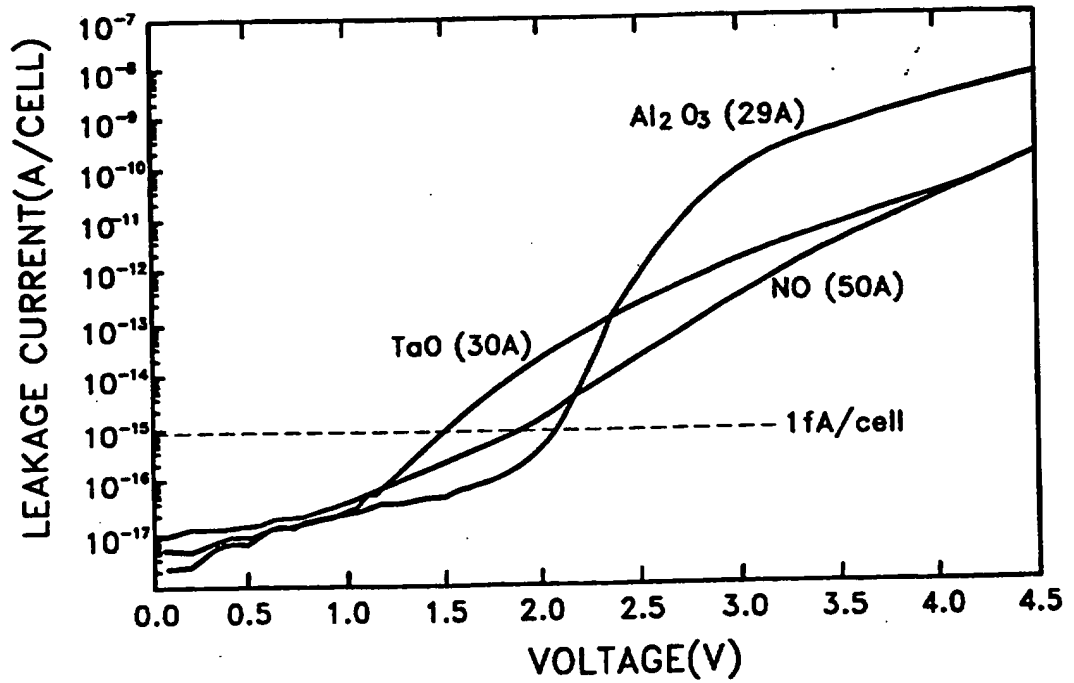


FIG. 21A

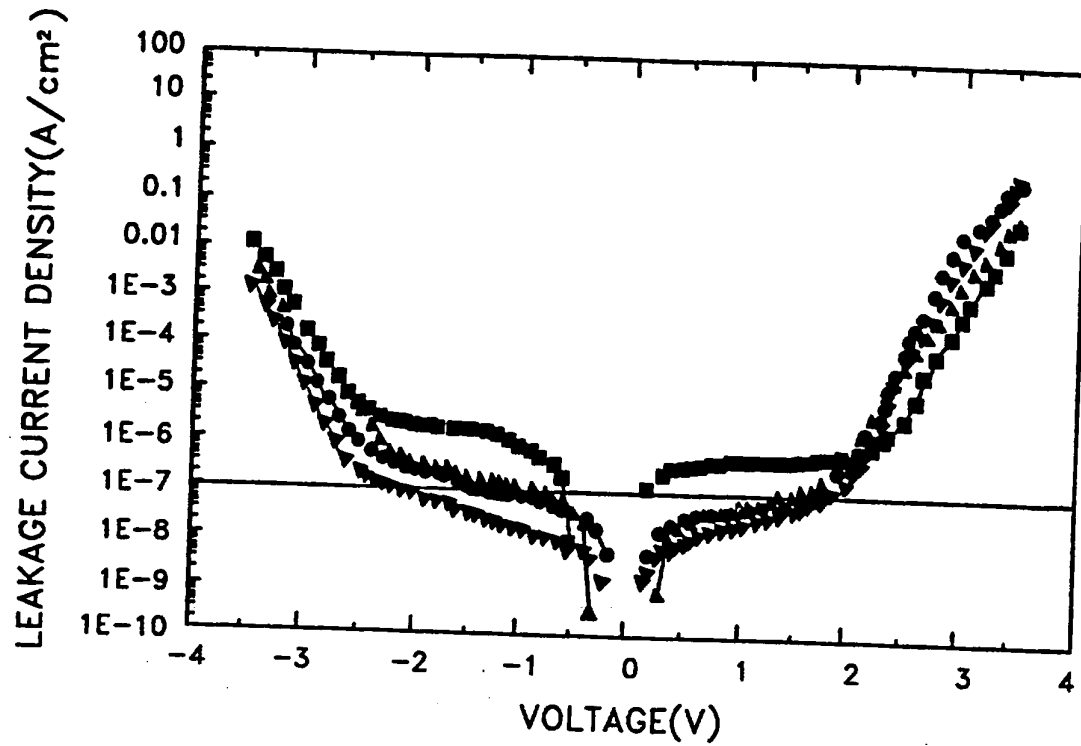


FIG. 21B

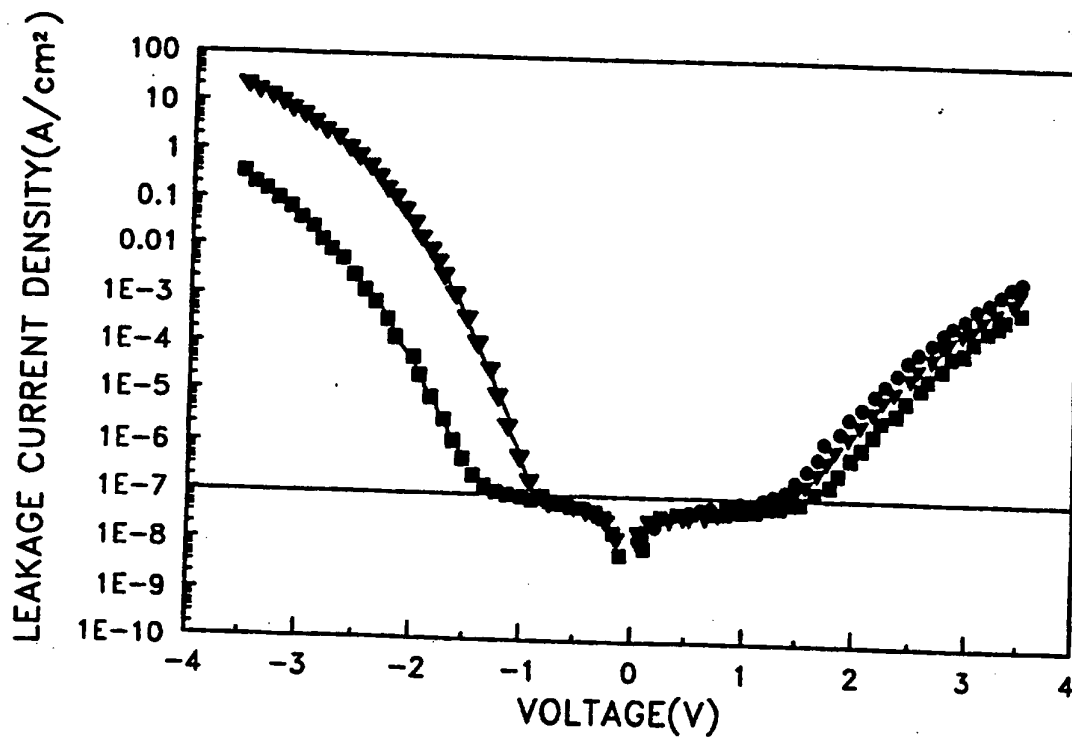
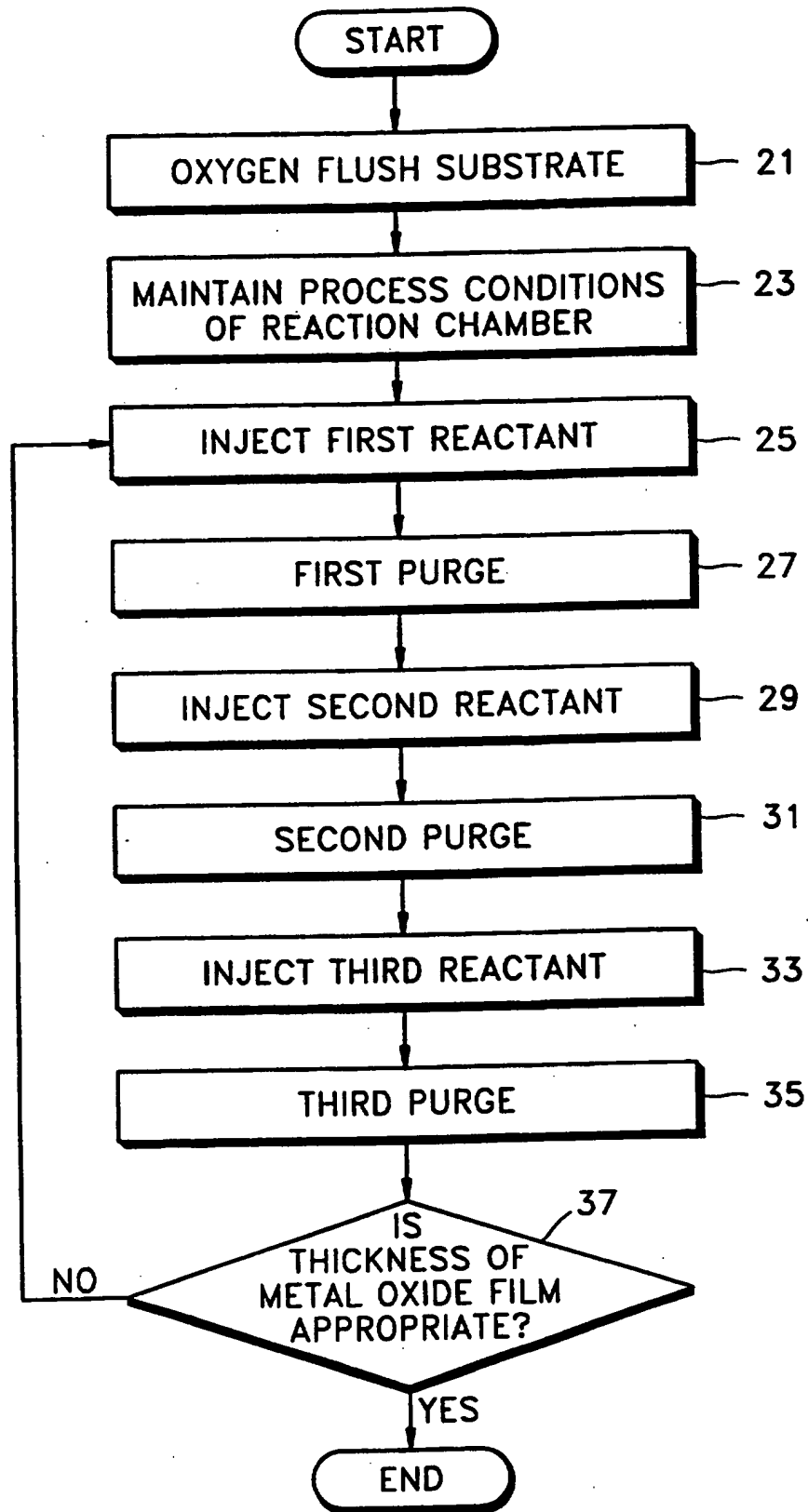




FIG. 22



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FIG. 23A

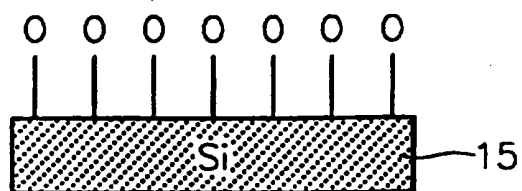


FIG. 23B

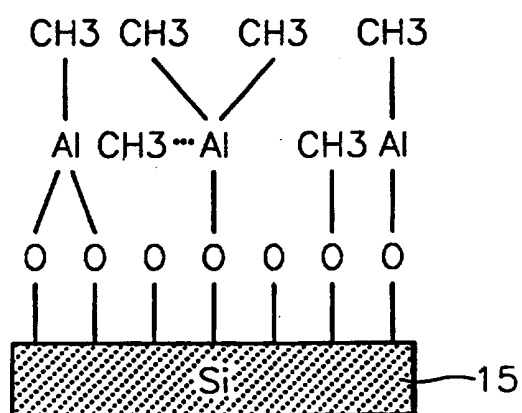
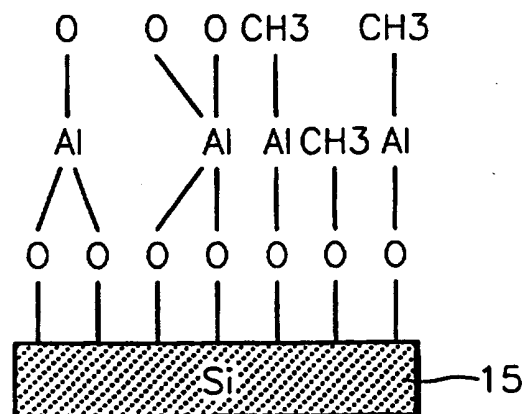


FIG. 23C



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FIG. 23D

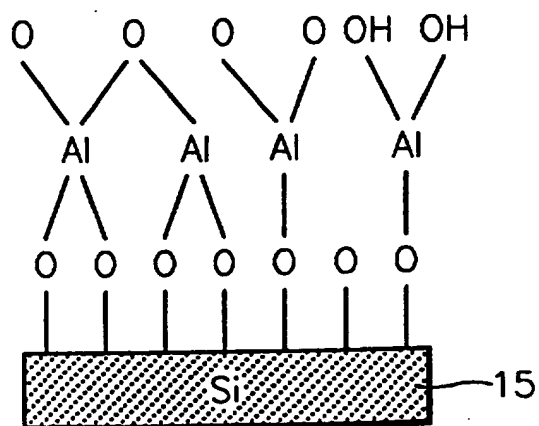


FIG. 24

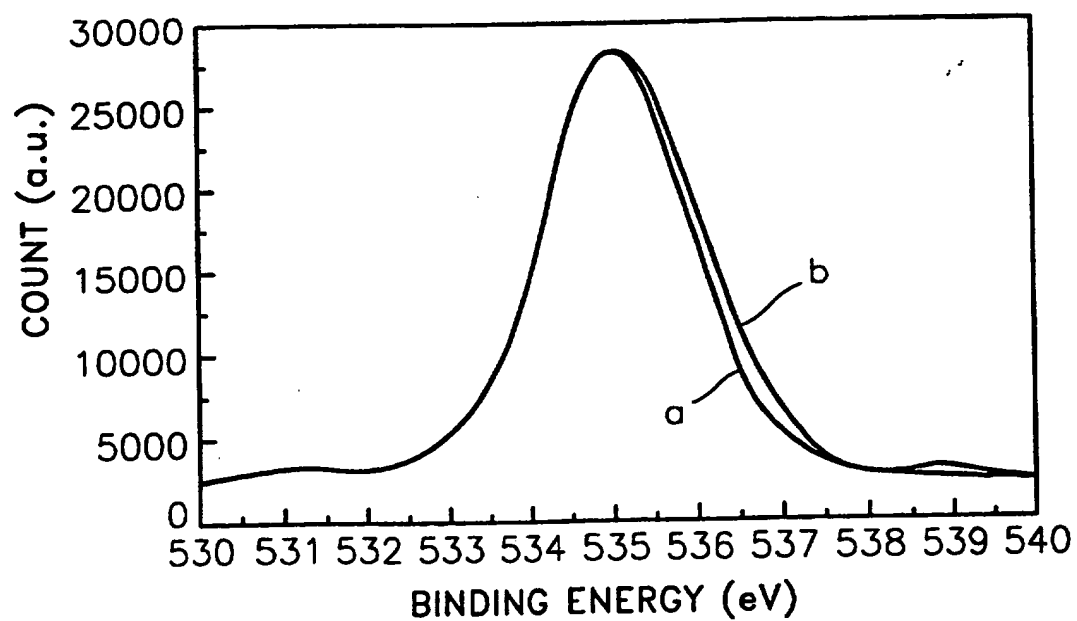


FIG. 25A

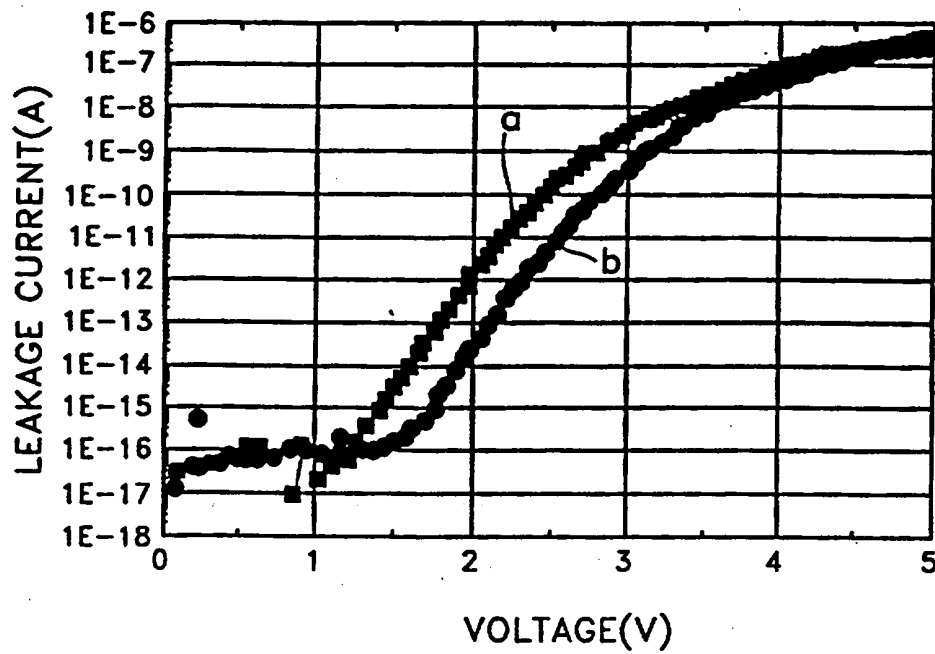


FIG. 25B

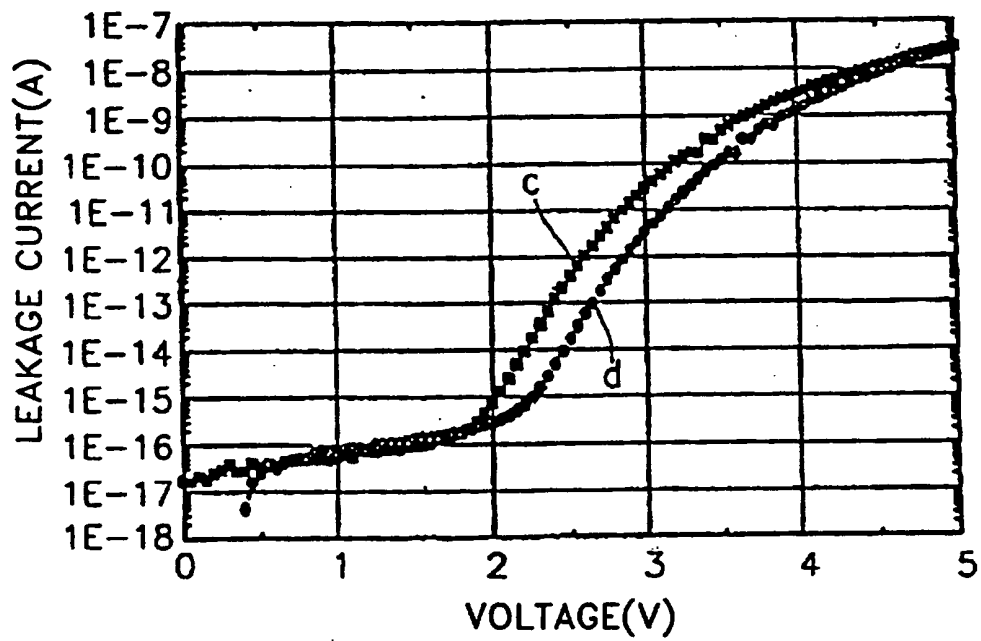


FIG. 26

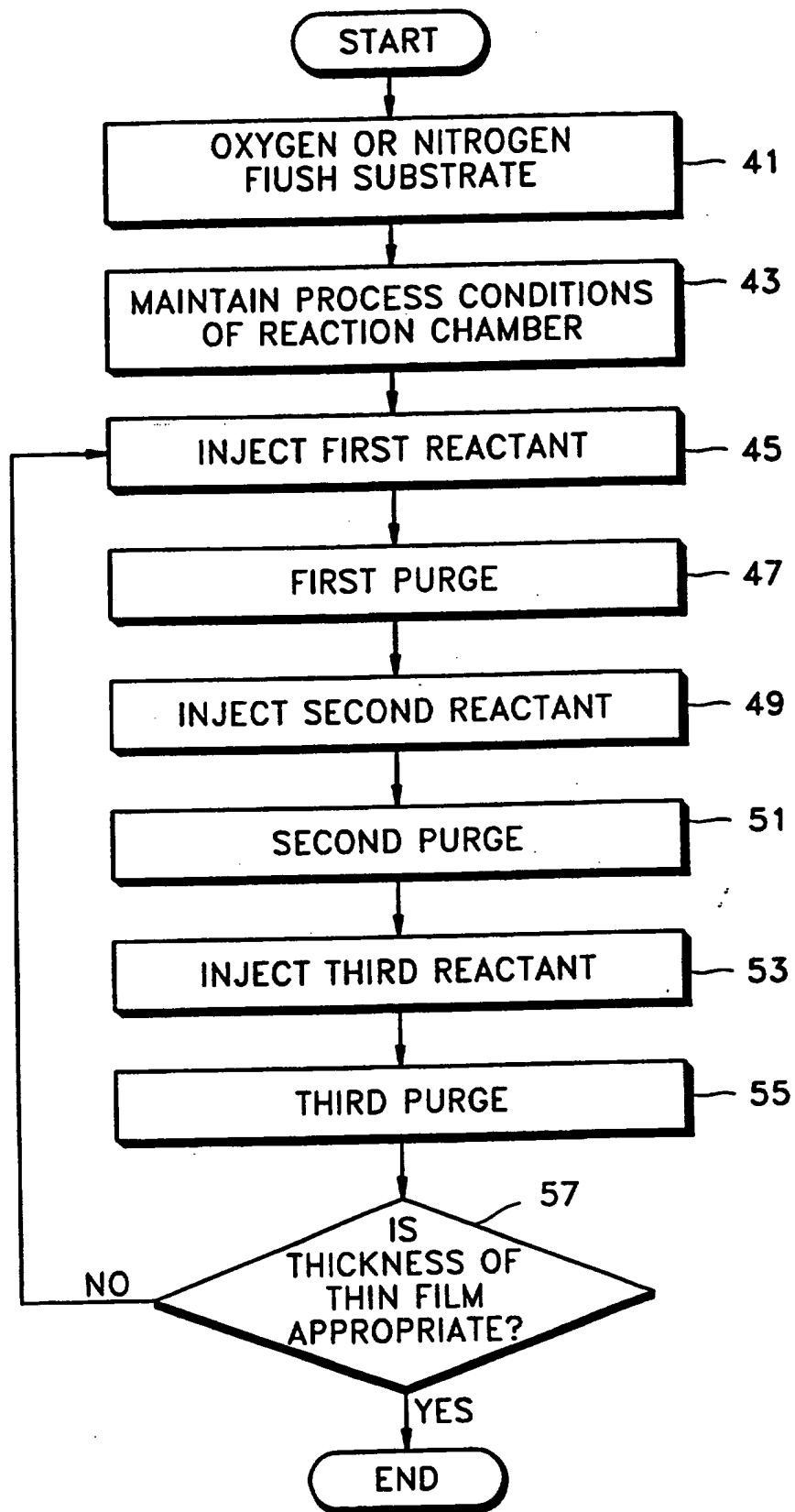


FIG. 27

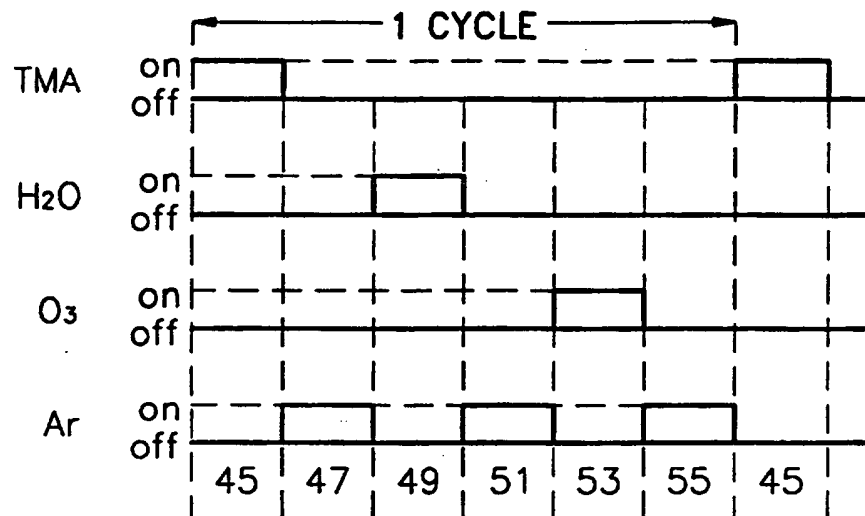
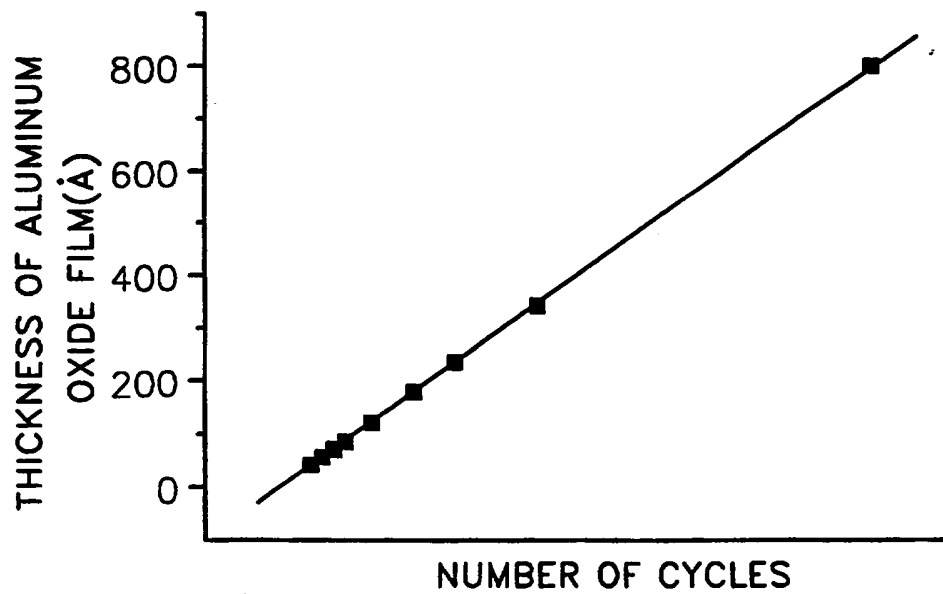


FIG. 28



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FIG. 29

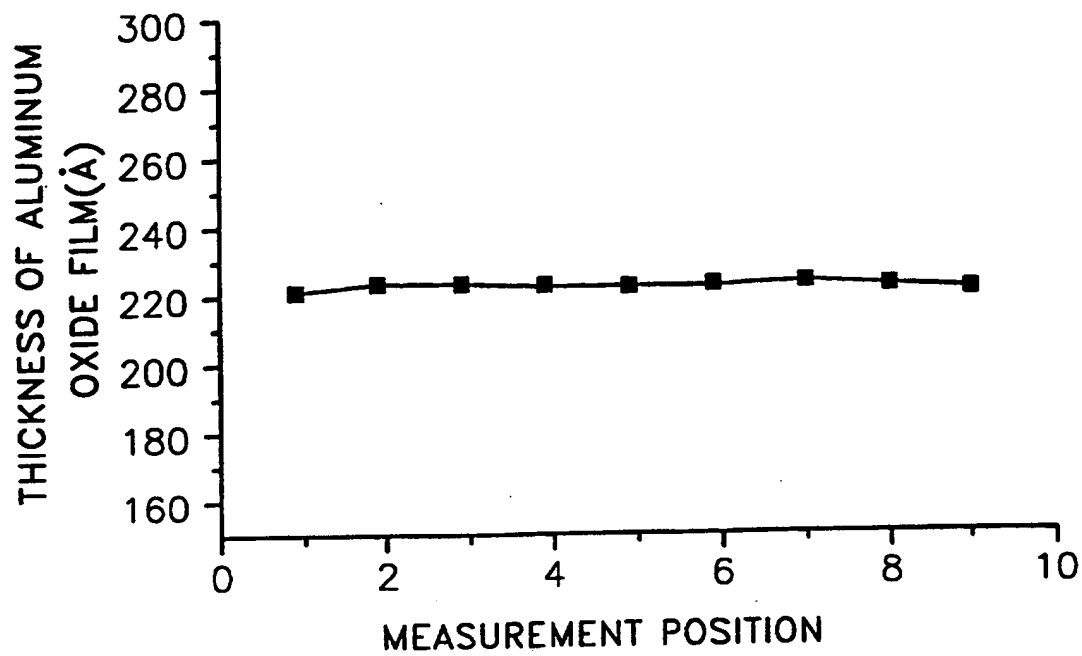


FIG. 30A

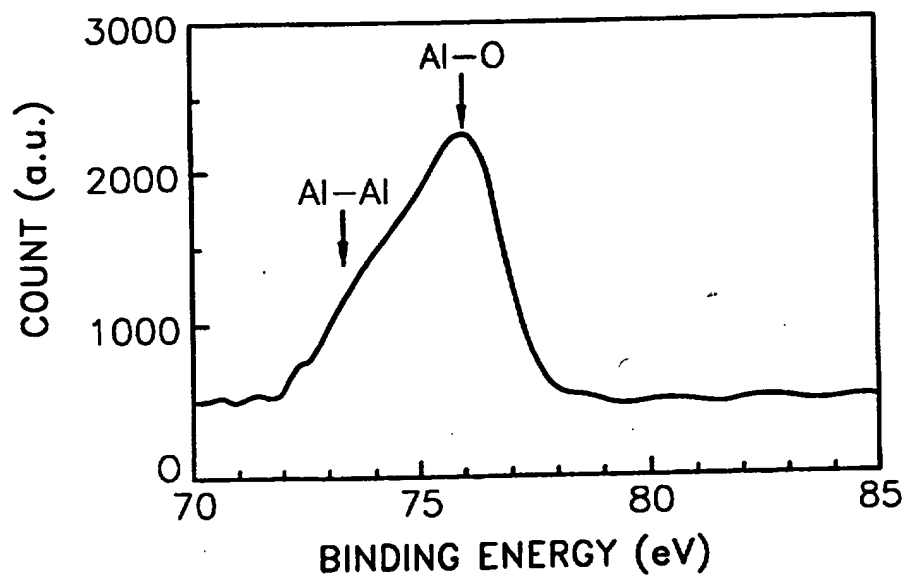


FIG. 30B

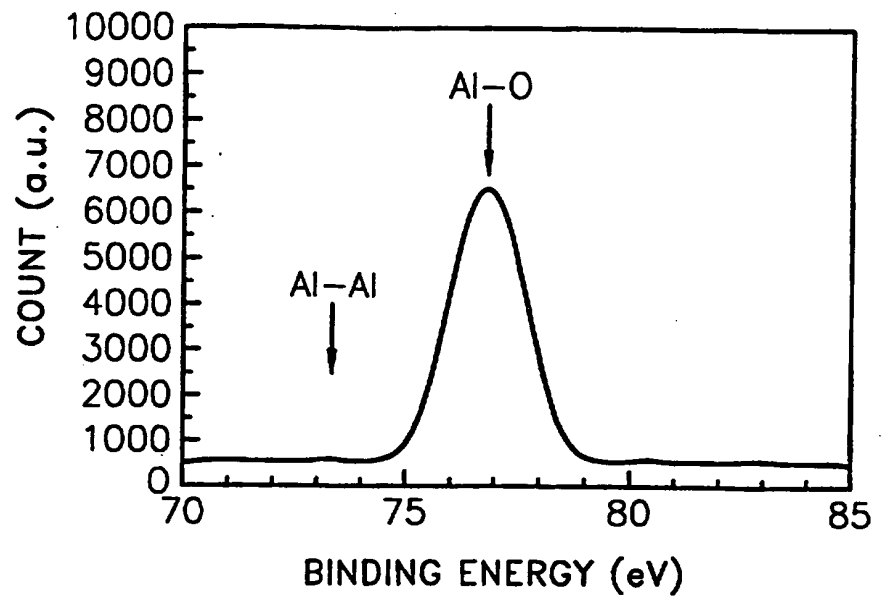


FIG. 31A

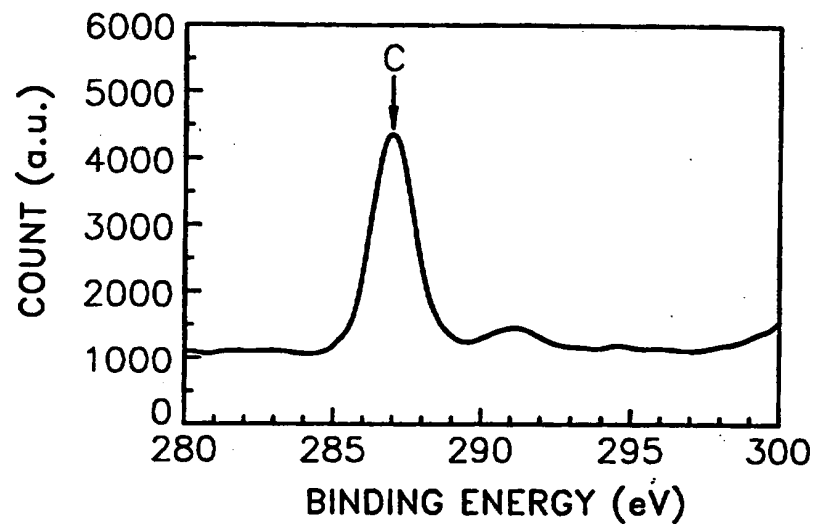


FIG. 31B

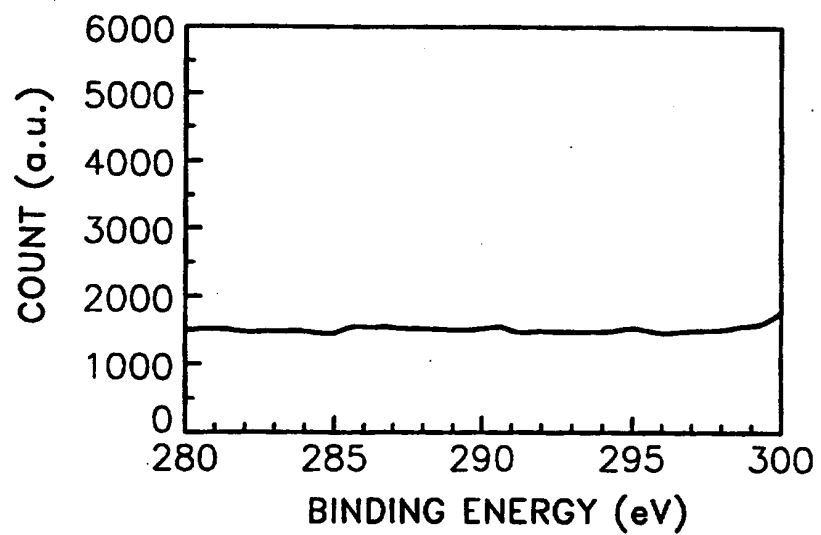
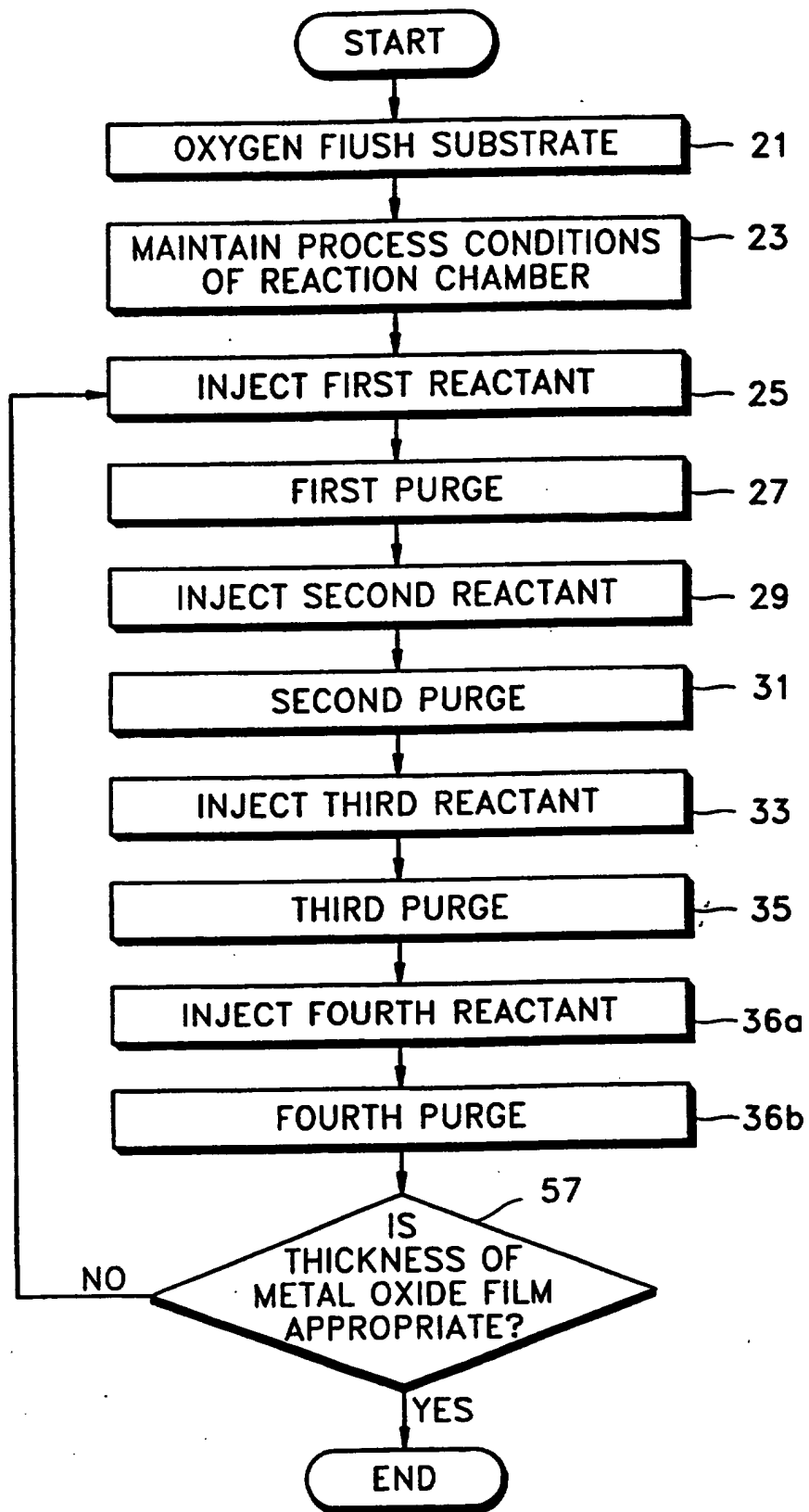




FIG. 32



# METHOD OF FORMING THIN FILM USING ATOMIC LAYER DEPOSITION METHOD

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention relates to a method of forming a thin film, and more particularly, to a method of forming a thin film using an atomic layer deposition (ALD) method.

### 2. Description of the Related Art

In general, a thin film is used as a dielectric of a semiconductor device, a transparent conductor of a liquid-crystal display, and a protective layer of an electroluminescent thin film display. A thin film may be formed by a sol-gel method, a sputtering method, an electroplating method, an evaporation method, a chemical vapor deposition (CVD) method, or an ALD method.

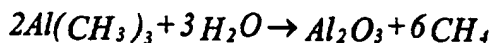
Among the methods, it is possible to obtain better step coverage by an ALD method than by the CVD method and it is possible to perform low temperature processing by the ALD method. In an ALD method, the thin film is formed by decomposing a reactant not by pyrolysis, but by chemical exchange through periodic supply of the respective reactants. Here, a method of forming an aluminum oxide film that can be used as a dielectric film of a semiconductor device using a conventional ALD method will be described in detail.

FIG. 1 is a flowchart of the process of forming an aluminum oxide film using a conventional ALD method. FIGS. 2A through 2D describe the reaction mechanism during the formation of the aluminum oxide film by the method of FIG. 1.

To be specific, a first reactant A, that is, trimethylaluminum ( $\text{Al}(\text{CH}_3)_3$ , "TMA") composed of aluminum  $a_1$  and a methyl ligand  $a_2$  is injected into a reaction chamber (not shown), into which a silicon substrate is loaded (step 1). The reaction chamber is purged of an physisorbed first reactant A by injecting an inert gas (step 3). Thus, only the first reactant A which is chemisorbed into a substrate S remains bonded to the substrate S as shown in FIG. 2A.

A second reactant B, water vapor consisting of oxygen  $b_1$  and a hydrogen radical  $b_2$ , is injected into a reaction chamber containing the substrate S into which the first reactant A is chemisorbed (step 5). By doing so, the second reactant B is chemisorbed into the first reactant A as shown in FIG. 2B.

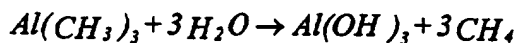
The hydrogen radical  $b_2$  of the chemisorbed second reactant B moves to the methyl ligand  $a_2$  of the first reactant A and the methyl ligand is separated from the first reactant A as shown in FIG. 2C. As shown in the chemical formula 1 and FIG. 2D, the hydrogen radical  $b_2$  of the second reactant B reacts with the methyl ligand  $a_2$  of the separated first reactant A and forms a volatile vapor phase material D formed of  $CH_4$ . An aluminum oxide film C is formed on the substrate S by the reaction between aluminum  $a_1$  of the first reactant A and



hydrogen  $b_1$  of the second reactant B.

The volatile vapor phase material D formed of  $CH_4$  and the un-reacted vapor are removed by purging the reaction chamber of the volatile vapor phase material D formed of  $CH_4$  and the vapor by injecting inert gas (step 7). It is checked whether the aluminum oxide film is formed to an appropriate thickness (step 9) and the steps 1 through 7 are cyclically repeated if necessary.

In a conventional ALD method, since the methyl ligand  $a_2$  is removed by the movement of the hydrogen radical  $b_2$ , sub-reaction occurs producing an OH radical that remains according to the movement of the hydrogen radical  $b_2$ , as described in the chemical



formula 2.

When the sub-reaction occurs, undesired impurities such as  $Al(OH)_3$  are included in the aluminum oxide film C. When impurities such as  $Al(OH)_3$  are included, it is not possible to obtain desired thin film characteristics. In particular, when an aluminum oxide film including  $Al(OH)_3$  is used as a dielectric film of a semiconductor device, the aluminum oxide film including  $Al(OH)_3$  operates as a trap site for electrons or a current leakage site, thus deteriorating the characteristics of the dielectric film.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method of forming a high purity thin film by suppressing the formation of undesired impurities when an atomic layer deposition (ALD) method is used.

To achieve the above object, in a method of forming a thin film using an atomic layer deposition (ALD) method according to an embodiment of the present invention, a first reactant including an atom that forms the thin film and a ligand is injected into a reaction chamber that comprises a substrate so that the first reactant is chemisorbed into the substrate. Any first reactant which is only physisorbed into the substrate is removed by purging the reaction chamber with inert gas. A thin film in units of atomic layers is formed by a chemical reaction between the atom that forms the thin film and a second reactant whose binding energy with respect to the atom that forms the thin film is larger than the binding energy of the ligand with respect to the atom that forms the thin film by injecting the second reactant into the reaction chamber and the ligand is removed without generating by-products.

According to the present invention, the ligand of the first reactant A is separated by the difference in binding energy without the movement of a radical from the second reactant B to the first reactant A. A volatile vapor phase material is formed by the combination of ligands and the vapor phase material is purged. Accordingly, since it is possible to reduce the impurities generated in the thin film by a sub-reaction without the movement of the radical, it is possible to obtain a high purity thin film.

In a method of forming a thin film using an ALD method according to another embodiment of the present invention, any first reactant which is only physisorbed is removed by chemisorbing the first reactant into the substrate and purging the reaction chamber with inert gas. The chemisorbed first reactant is chemically exchanged to form a metal-oxygen atomic layer film by injecting a second reactant which does not contain a hydroxide into the reaction chamber. The physisorbed second reactant is removed by purging the reaction chamber with inert gas. A metal oxide film in units of atomic layers is formed while the generation of a hydroxide is prevented by injecting a third reactant into the reaction chamber, thus chemically exchanging the remaining chemisorbed first reactant to further contribute to the formation of the metal-oxygen atomic layer. After injecting the third reactant into the reaction chamber, a fourth reactant such as ozone gas for removing impurities and improving

the stoichiometry of the metal oxide film can be injected into the reaction chamber and the reaction chamber can be purged with inert gas.

It is preferable that the first reactant is a metal reactant, that the second reactant which does not contain a hydroxide is  $N_2O$ ,  $O_2$ ,  $O_3$ , or  $CO_2$ , and that the third reactant is oxidizing gas. The temperature of the reaction chamber is preferably maintained to be between 100 and 400°C from the step of injecting the first reactant to the step of injecting the third reactant. The dangling bond of the surface of the substrate can be terminated by injecting oxidizing gas before injecting the first reactant, when the substrate is a silicon substrate.

In a method of forming a thin film using an ALD method according to another embodiment, any first reactant which is only physisorbed into the substrate is removed by chemisorbing the first reactant into the substrate and purging the reaction chamber with inert gas. A thin film in units of atomic layers is formed by injecting a second reactant into the reaction chamber and chemically exchanging the first reactant to further contribute to the formation of the second reactant. A third reactant for removing impurities and improving the stoichiometry of the thin film is injected into the reaction chamber in which the thin film is formed after removing any physisorbed second reactant by purging the reaction chamber with inert gas.

It is preferable that the first reactant is a metal reactant and that the second and third reactants are oxidizing gases. It is preferable that the first reactant is a metal reactant and that the second and third reactants are nitriding gases. The dangling bond of the surface of the substrate can be terminated by injecting oxidizing gas or nitriding gas before injecting the first reactant, when the substrate is a silicon substrate. The temperature of the reaction chamber is maintained to be between 100 and 400°C from the step of injecting the first reactant to the step of injecting the third reactant.

According to the method of forming the atomic layer thin film of the present invention, it is possible to prevent or suppress the formation of an undesired by-product such as hydroxide, to thus obtain a high purity thin film.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

The above object and advantages of the present invention will become more apparent by describing in detail a preferred embodiment thereof with reference to the attached drawings in which:

FIG. 1 is a flowchart of the process of forming an aluminum oxide film using a conventional atomic layer deposition (ALD) method;

FIGS. 2A through 2D illustrate the reaction mechanism during the formation of the aluminum oxide film of FIG. 1;

FIG. 3 schematically illustrates an apparatus for forming an atomic layer thin film by an ALD method according to the present invention;

FIGS. 4A through 4D illustrate the reaction mechanism of a method of forming a thin film using an ALD method according to a first embodiment of the present invention;

FIG. 5 is a flowchart of the process of forming an aluminum oxide film according to the first embodiment of the present invention;

FIGS. 6A through 6D illustrate the reaction mechanism when the aluminum oxide film is formed using the ALD method of FIG. 5;

FIGS. 7 and 8 are graphs showing residual gas analysis (RGA) data when the aluminum oxide film is formed by the conventional technology and the first embodiment of the present invention, respectively;

FIG. 9 is a graph showing the thickness of the aluminum oxide film according to the number of cycles when the aluminum oxide film is formed by the conventional technology and the first embodiment of the present invention;

FIG. 10 is a graph showing stress hysteresis according to the temperature of aluminum oxide films formed by the conventional technology and the first embodiment of the present invention;

FIG. 11 is a graph showing a percentage of contraction of thickness according to the post-annealing conditions of aluminum oxide films formed by the conventional technology and the first embodiment of the present invention;

FIGS. 12 and 13 are graphs showing absorption constants and indices of refraction of aluminum oxide films formed by the conventional technology and the first embodiment of the present invention according to wavelength;

FIG. 14 is a graph showing wet etch rates of aluminum oxide films formed by the conventional technology and the first embodiment of the present invention according to post-annealing temperature and the atmosphere gas;

FIG. 15 is a sectional view showing the structure of a capacitor of a semiconductor device, for which a dielectric film formed by the first embodiment of the present invention is used;

FIG. 16 is a sectional view showing the structure of a transistor of a semiconductor device, for which a dielectric film formed by the first embodiment of the present invention is used;

FIG. 17 is a graph illustrating the leakage current characteristics of a conventional capacitor and a SIS capacitor, for which a dielectric film formed by the first embodiment of the present invention is used, according to applied voltage;

FIG. 18 is a graph showing the takeoff voltage of the SIS capacitor, for which a dielectric film formed by the first embodiment of the present invention is used, according to the thickness of an equivalent oxide film;

FIG. 19 is a graph showing the leakage current characteristic of a MIS capacitor, for which a dielectric film formed by the first embodiment of the present invention is used, according to applied voltage;

FIG. 20 is a graph for comparing the leakage current characteristic of the MIS capacitor, for which a dielectric film formed by the first embodiment of the present invention is used, with the leakage current characteristic of a conventional capacitor;

FIGS. 21A and 21B are graphs showing leakage current characteristics according to applied voltage when the aluminum oxide films according to the conventional technology and the first embodiment of the present invention are used as capping films of a MIM capacitor;

FIG. 22 is a flowchart of a second embodiment of the method of forming a thin film using an ALD method according to the present invention;

FIGS. 23A through 23D illustrate a combination relationship between reactants adsorbed on a substrate when an aluminum oxide film is formed by a method of forming a thin film using an ALD method according to the second embodiment of the present invention;

FIG. 24 is an x-ray photoelectron spectroscopy (XPS) graph of the aluminum oxide film formed by a conventional ALD method;

FIGS. 25A and 25B are graphs for showing the leakage current characteristics of aluminum oxide films manufactured by the conventional method and the second embodiment of the present invention, respectively;

FIG. 26 is a flowchart of a method of forming a thin film using an ALD method according to a third embodiment of the present invention;

FIG. 27 is a timing diagram showing the supply of reactants during the formation of a thin film using an ALD method according to the third embodiment of the present invention;

FIG. 28 is a graph showing the thickness of an aluminum oxide film manufactured by the method of forming an atomic layer thin film according to the third embodiment of the present invention as a function of the number of times the steps of the method are repeated;

FIG. 29 is a graph for showing the uniformity of an aluminum oxide film manufactured by the method of forming an atomic layer thin film according to the third embodiment of the present invention;

FIGS. 30A and 30B are graphs for analyzing the aluminum peaks of aluminum oxide films manufactured by the conventional technology and the method of forming an atomic layer thin film according to the third embodiment of the present invention, respectively, using XPS;

FIGS. 31A and 31B are graphs for analyzing the carbon peaks of aluminum oxide films manufactured by the conventional technology and the method of forming a thin film using an ALD method according to the third embodiment of the present invention, respectively, using XPS; and

FIG. 32 is a flowchart of a method of forming an atomic layer thin film according to a fourth embodiment of the present invention.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention now will be described more fully with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art. In the drawings, the thickness of layers and regions are exaggerated for clarity. It will also be understood that when a layer is referred to as being



"on" another layer or substrate, it can be directly on the other layer or substrate, or intervening layers may also be present. The same reference numerals in different drawings represent the same elements, and elements will only be described once.

FIG. 3 illustrates an apparatus for forming an atomic layer thin film using an atomic layer deposition (ALD) method according to the present invention. The apparatus includes a reaction chamber 11 that can be heated by an external heater (not shown), a susceptor 13 installed at the bottom of the reaction chamber 11 to support a substrate 15, for example, a silicon substrate thereon, a shower head 17 installed above the susceptor 13 so that reaction gas may be injected into the reaction chamber 11, and a vacuum pump 19 connected to the reaction chamber 11 in order to control the pressure inside the reaction chamber 11.

Two gas inlets A and B, which are separated from each other, are connected to the shower head 17. A first reactant, inert gas, a second reactant, and a third reactant can be injected into the shower head 17. The first reactant is a metal reactant. The Inert gas is nitrogen gas or argon gas. The second reactant is oxidizing gas which does not contain a hydroxide, for example,  $N_2O$ ,  $O_2$ ,  $O_3$ , or  $CO_2$  gas or water vapor. The third reactant is water vapor or a material that includes an oxygen radical as an activated oxidizing agent, such as ozone,  $O_2$  plasma or  $N_2O$  plasma. In FIG. 3, the second reactant and the third reactant are installed separately, however, they can be installed together.

The first reactant and inert gas are injected into the reaction chamber 11 through the gas inlet A. The second reactant and the third reactant are injected into the reaction chamber 11 through the gas inlet B. The first reactant, the second reactant, and the third reactant have different gas inlets in order to prevent them from reacting with each other inside a gas inlet. The injection of the first reactant and inert gas into the reaction chamber 11 is controlled by a first valve V1 and a second valve V2. The injection of the second reactant and the third reactant into the reaction chamber 11 is controlled by a third valve V3 and a fourth valve V4.

Various embodiments of a method according to the present invention of forming an atomic layer thin film using the above-described apparatus will now be described.

#### First Embodiment

FIGS. 4A through 4D illustrate the reaction mechanism of a method of forming a thin film using an ALD method according to a first embodiment of the present invention. After a first reactant A, consisting of an atom  $a_1$  that forms a thin film and a ligand  $a_2$ , is chemisorbed

into a substrate 15, for example, a silicon substrate, by injecting the first reactant A into a reaction chamber 11 into which the substrate is loaded, the physisorbed first reactant A is removed by purging the reaction chamber by injecting the inert gas (FIG. 4A).

A second reactant B is injected into the reaction chamber 11 containing the substrate into which the first reactant A is adsorbed. By doing so, the second reactant B is chemisorbed into the first reactant A. An imperfect material that actively reacts with the first reactant A is used as the second reactant B. A material, in which the binding energy between the second reactant B and the thin film forming atom  $a_1$  of the first reactant A is larger than the binding energy between the thin film forming atom  $a_1$  of the first reactant A and the ligand  $a_2$ , is used as the second reactant B (FIG. 4B).

Since the binding energy between the second reactant B and the thin film forming atom  $a_1$  of the first reactant A is larger than the binding energy between the thin film forming atom  $a_1$  of the first reactant A and the ligand  $a_2$ , the second reactant B is combined with the thin film forming atom  $a_1$  of the first reactant A and the ligand  $a_2$  is separated from the first reactant A (FIG. 4C).

Since the ligand  $a_2$  separated from the first reactant A is unstable, a volatile vapor phase material D is formed by combination of the ligands  $a_2$ . A thin film C in units of atomic layers is formed on the substrate 15 by a reaction between the thin film forming atom  $a_1$  of the first reactant A and the second reactant B. The volatile vapor phase material D is removed by purging with the inert gas (FIG. 4D).

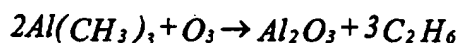
A case where the method of forming a thin film using a difference in binding energy, which is described in FIGS. 4A through 4D, is applied to forming an aluminum oxide film will be taken as an example.

FIG. 5 is a flowchart of the process of forming an aluminum oxide film according to a first embodiment of the present invention. FIGS. 6A through 6D illustrate the reaction mechanism when the aluminum oxide film is formed using the ALD method of FIG. 5. The first reactant A such as trimethyl aluminum ( $\text{Al}(\text{CH}_3)_3$ , TMA) consisting of thin film forming aluminum  $a_1$  and a methyl ligand  $a_2$  is injected into the reaction chamber 11, into which the substrate 15, for example, a silicon substrate, is loaded (step 101). The physically adsorbed TMA is removed by purging with inert gas (step 103). By doing so, only TMA that is chemisorbed into the substrate 15 as shown in FIG. 6A remains.

The second reactant such as ozone B that is an oxidizing agent is injected into the reaction chamber 11, into which the TMA is adsorbed (step 105). By doing so, ozone B is chemisorbed into aluminum  $a_1$  of the TMA as shown in FIG. 6B.

Ozone B is an imperfect material that actively reacts with TMA. The binding energy between ozone B and aluminum  $a_1$  of the TMA is about 540 kJ/mol, which is larger than the binding energy between aluminum  $a_1$  of the TMA and the methyl ligand  $a_2$  (for example, Al-C binding energy) which is 255 kJ/mol. Since the binding energy between ozone B and thin film forming aluminum  $a_1$  of the TMA is larger than the binding energy between thin film forming aluminum  $a_1$  of the TMA and the methyl ligand  $a_2$ , the methyl ligand  $a_2$  is separated from the TMA as shown in FIG. 6C.

Also, since the methyl ligand  $a_2$  separated from the TMA is unstable, a volatile vapor phase material D formed of  $C_2H_6$  is formed by the combination of the methyl ligands  $a_2$  as shown in FIG. 6D. An aluminum oxide film C in units of atomic layers is formed on the substrate 15 by the reaction between thin film forming aluminum  $a_1$  of the TMA and ozone B



as shown in the chemical formula 3.

The volatile vapor phase material D formed of  $C_2H_6$  and the un-reacted methyl ligands  $a_2$  are removed by purging the reaction chamber a second time with the inert gas (step 107). It is checked whether the aluminum oxide film is formed to an appropriate thickness (step 109) and the steps 101 through 107 are cyclically repeated if necessary.

Ozone is used as the second reactant in the present embodiment. However, ozone can be activated more using ultraviolet (UV) rays, or  $O_2$  plasma or  $N_2O$  plasma can be used as the



activated oxidizing agent instead of ozone as shown in the chemical formula 4.

FIGS. 7 and 8 are graphs showing residual gas analysis (RGA) data when an aluminum oxide film is formed by the conventional technology and the first embodiment of the present invention, respectively. In FIGS. 7 and 8, the aluminum oxide film is formed in the sections marked with arrows.

Since the form of the removed ligand varies according to the mechanism with which the second reactant B reacts with the first reactant A as mentioned above, the material generated during a process varies. Namely, when the TMA and water vapor ( $\text{H}_2\text{O}$ ) are used as the first reactant A and the second reactant B, respectively, as in the case for FIG. 7,  $\text{CH}_3^+$  and  $\text{CH}_2^+$ , which are formed by receiving a hydrogen radical from water vapor ( $\text{H}_2\text{O}$ ), are detected as the main by-products. When the TMA and ozone are used as the first reactant A and the second reactant B, respectively, as is the case for FIG. 8,  $\text{CH}_3$  ligands are removed, and thus  $\text{C}_2\text{H}_5^+$  or  $\text{C}_2\text{H}_6^+$  is detected as a main by-product.

FIG. 9 is a graph showing the thickness of the aluminum oxide film according to the number of cycles when the aluminum oxide film is formed by the conventional technology and the first embodiment of the present invention. The thickness of a deposited thin film is determined by the number of supply cycles of each reactant since an atomic layer deposition (ALD) method is a surface controlling process. Namely, when the thickness increases linearly with the number of cycles, it means that the thin film is formed by an ALD method. As shown in FIG. 9, since the thickness linearly increases in the conventional technology and in the present invention, it is noted that the thin film is formed by an ALD method.

The difference in latent cycles between the conventional technology (marked with ●), in which water vapor is used as the second reactant B, and the present invention (marked with ○), in which ozone is used as the second reactant B is shown. Namely, the thin film is deposited from an initial cycle without a latent cycle in the present invention (marked with ○). However, the thin film is deposited after the lapse of a latent period of 12 cycles in the conventional technology (marked with ●). From this, it is noted that the aluminum oxide film is more stably formed in the present invention since the thin film is formed by a heterogeneous reaction.

FIG. 10 is a graph showing the stress hysteresis according to the temperature of aluminum oxide films formed by the conventional technology and the first embodiment of the present invention.

To be specific, in the stress hysteresis (marked with □) of the conventional aluminum oxide film formed by using TMA as the first reactant A and using water vapor as the second reactant B, the form of stress changes from tensile stress into compression stress at  $450^\circ\text{C}$ . Meanwhile, in the stress hysteresis (marked with ●) of the aluminum oxide film according to the present invention, which is formed by using the TMA and ozone as the first reactant A

and the second reactant B, respectively, the form of stress is tensile stress throughout the entire temperature range, that is, a stress mode does not change. Accordingly, it is noted that the film formed according to the present invention is more stable against heat.

FIG. 11 is a graph showing a percentage of contraction of thickness according to the post-annealing conditions of the aluminum oxide films formed by the conventional technology and the first embodiment of the present invention. On the X axis, N450, N750, and N830 are samples post annealed in nitrogen atmospheres at 450°C, 750°C, and 830°C, respectively. O450, O750, and O830 are samples post annealed in oxygen atmospheres at 450°C, 750°C, and 830°C, respectively. RTO is a sample, on which rapid thermal oxidation is performed at 850°C. It is noted that the percentage of thickness contraction (the decreasing rate of thickness) according to the temperature and gas conditions of the post-annealing in the aluminum oxide films does not significantly vary according to whether the films were formed by the conventional technology or the first embodiment of the present invention.

FIGS. 12 and 13 are graphs showing absorption constants and indices of refraction of the aluminum oxide films formed by the conventional technology and the first embodiment of the present invention according to wavelength. The absorption constants of the aluminum oxide films formed by the conventional technology and the first embodiment of the present invention are less than 0.005 for wavelengths of 180 through 900 nm as shown in FIG. 12. That is, the aluminum oxide films formed by the conventional technology and the first embodiment of the present invention show excellent transparency. The indices of refraction of the aluminum oxide films formed by the conventional technology and the first embodiment of the present invention do not significantly vary for wavelengths of 180 through 900 nm as shown in FIG. 13.

FIG. 14 is a graph showing wet etch rates of aluminum oxide films formed by the conventional technology and the first embodiment of the present invention according to post-annealing temperature and the atmosphere gas. On the X axis, as-dep is a sample that is not annealed after being deposited on the substrate. N450, N750, and N830 are sample that are post-annealed in nitrogen atmospheres at 450°C, 750°C, and 830°C. O450, O750, and O830 are samples that are post-annealed in oxygen atmospheres at 450°C, 750°C, and 830°C. RTP is a sample that underwent rapid thermal oxidation in an oxygen atmosphere at 850°C. The Y axis denotes etch rates when the respective samples are wet etched by a 200:1 HF solution.

As shown in FIG. 14, in the aluminum oxide films formed by the conventional technology and the first embodiment of the present invention, wet etch rates are reduced as annealing temperatures increase regardless of annealing conditions. In particular, when post-annealing is performed at temperatures higher than 800°C, the etch rate is rapidly reduced to 2 through 3 Å/min. Also, when post-annealing is performed at temperatures lower than 800°C, the etch rate of the aluminum oxide film according to the first embodiment of the present invention is lower than the etch rate of the aluminum oxide film according to the conventional technology by about 30%. From this, it is noted that the oxide film is more chemically stable when ozone is used as an oxidizing gas than when water vapor is used as the oxidizing gas.

A case where the aluminum oxide film formed by the first embodiment of the present invention is used for a semiconductor device, will now be described.

FIG. 15 is a sectional view showing the structure of a capacitor of a semiconductor device, for which a dielectric film formed by the first embodiment of the present invention is used. The capacitor of the semiconductor device, for which the dielectric film formed by the first embodiment of the present invention is used, includes a lower electrode 205 formed on a substrate 201, for example, a silicon substrate, a dielectric film 207, and an upper electrode 209. In FIG. 15, reference numerals 203 and 211 denote an interlayer dielectric film and a capping layer formed on the upper electrode of the capacitor, respectively.

Hereinafter, a capacitor, in which the upper electrode 209 and the lower electrode 205 are formed of a polysilicon film doped with impurities and the dielectric film 207 is formed of an aluminum oxide film formed by the first embodiment of the present invention, is referred to as an "SIS capacitor". A capacitor, in which the lower electrode 205 is formed of a polysilicon film doped with the impurities, the dielectric film 207 is formed of an aluminum oxide film formed by the first embodiment of the present invention, and the upper electrode 209 is formed of a TiN film, is referred to as a "MIS capacitor". A capacitor, in which the upper electrode 209 and the lower electrode 205 are formed of noble metals of the platinum group, such as Pt and Ru, and the dielectric film 207 is formed of an insulating film such as a TaO film or BST(BaSrTiO<sub>3</sub>), is referred to as a "MIM capacitor".

FIG. 16 is a sectional view showing the structure of a transistor of a semiconductor device, for which a dielectric film formed by the first embodiment of the present invention is used. The semiconductor device, for which the dielectric film according to the first

embodiment of the present invention is used includes a silicon substrate 301 doped with impurities such as phosphorus, arsenic, boron, which operates as a first electrode, a gate insulating film 305, which operates as a dielectric film, and a gate electrode 307, which operates as a second electrode. In FIG. 2, reference numeral 303 denotes source and drain regions, which are impurity doped regions.

When the structure of the transistor of the semiconductor device according to the present invention is compared with the structure of the capacitor of the semiconductor device according to the present invention, the silicon substrate 301 and the gate electrode 307 correspond to the lower electrode and the upper electrode, respectively. The gate insulating film 305 corresponds to the dielectric film of the capacitor.

The insulating characteristics of the dielectric film will now be described with reference to the structure of the capacitor for convenience of explanation, however, the same treatment applies to the transistor.

FIG. 17 is a graph illustrating the leakage current characteristics of a conventional capacitor and a SIS capacitor, for which the dielectric film formed by the first embodiment of the present invention is used, according to applied voltage.

To be specific, the SIS capacitor according to the present invention (marked with ○) is the same as the conventional capacitor (marked with ●), except that the method of forming the dielectric film of the SIS capacitor is different from the method of forming the dielectric film of the conventional capacitor. As shown in FIG. 17, the SIS capacitor according to the present invention (○) shows a take off voltage larger than the take off voltage of the conventional capacitor (●) at a leakage current density that can be allowed in a capacitor of a common semiconductor device, that is,  $1\text{E-}7\text{A}/\text{cm}^2$ . Therefore, since the thickness of the dielectric film can be reduced at a certain leakage current value in the SIS capacitor according to the present invention (○), the SIS capacitor according to the present invention (○) is advantageous for increasing the degree of integration of the semiconductor device.

FIG. 18 is a graph showing the takeoff voltage of the SIS capacitor, in which the dielectric film formed by the first embodiment of the present invention is used, according to the thickness of an equivalent oxide film. Since the SIS capacitor according to the present invention shows stable insulating characteristics until the thickness of the equivalent oxide film is 35Å, the takeoff voltage is not significantly reduced. When the thickness of the

equivalent oxide film is less than 35Å, the takeoff voltage is rapidly reduced, and thus the insulating characteristics deteriorate.

FIG. 19 is a graph for showing the leakage current characteristic of a MIS capacitor, for which the dielectric film formed by the first embodiment of the present invention is used, according to applied voltages. As a common reference value, when a leakage current density is  $1 \times 10^{-7}$  and a voltage is 1.2V, the thickness of the equivalent oxide film can be 26.5Å in the case of the MIS capacitor according to the present invention. When the thickness of the equivalent oxide film is reduced, it is very advantageous for increasing the degree of integration of the semiconductor device.

FIG. 20 is a graph for comparing the leakage current characteristic of the MIS capacitor, for which the dielectric film formed by the first embodiment of the present invention is used, with the leakage current characteristic of the conventional capacitor. The conventional capacitor is the same as the MIS capacitor according to the present invention, excluding that the dielectric film of the conventional capacitor is different from the dielectric film of the MIS capacitor. As shown in FIG. 20, an applied voltage in the MIS capacitor, for which the aluminum oxide film according to the first embodiment of the present invention is used, is larger than an applied voltage in the conventional capacitor, in which a TaO film or a NO film is used as the dielectric film, in the leakage current value of 1fA per a cell. That is to say, the leakage current characteristic of the MIS capacitor according to the present invention is better, even in a thin equivalent oxide film, than the leakage current characteristic of the conventional capacitor. In FIG. 20, numbers in parentheses denote the thicknesses of the dielectric films.

FIGS. 21A and 21B are graphs showing leakage current characteristics according to applied voltage when the aluminum oxide films according to the conventional technology and the first embodiment of the present invention are used as the capping films of a MIM capacitor. In FIGS. 21A and 21B, "■" denotes the MIM capacitor when the capping film is not used. In FIG. 21A, "●" denotes a case where the aluminum oxide film is formed to be the capping film according to the conventional technology. "▽" denotes a case where the aluminum oxide film formed to be the capping film is hydrogen annealed at 400°C. In FIG. 21B, "●" denotes a case where the aluminum oxide film is formed to be the capping film according to the first embodiment of the present invention. "Δ" denotes a case where the aluminum oxide film formed to be the capping film is hydrogen annealed at 400°C. "▽"



denotes a case where the aluminum oxide film formed to be the capping film is nitrogen annealed at 700°C.

In general, when the MIM capacitor is used for a semiconductor device, the dielectric film deteriorates during the hydrogen annealing, which is performed in a successive alloy process. Accordingly, the capping film that operates as a hydrogen barrier is formed on the MIM capacitor. As shown in FIG. 21A, when the aluminum oxide film formed by the first embodiment of the present invention is used as the capping film, the leakage current characteristic does not deteriorate since a barrier characteristic is excellent after the successive hydrogen annealing processes are performed. However, when the aluminum oxide film formed by the conventional technology is used as the capping film as shown in FIG. 21B, hydrogen of water vapor and an OH ligand deteriorate the leakage current characteristic of the MIM capacitor during the deposition process.

### Second Embodiment

FIG. 22 is a flowchart of a second embodiment of the method of forming a thin film using an ALD method according to the present invention. A termination treatment of combining the dangling bond of the substrate 15 with oxygen is performed by oxygen flushing the substrate (15 of FIG. 3), for example, the silicon substrate, with oxidizing gas (step 21). That is, at any sites where oxygen can be bonded to the substrate 15, oxygen is bonded to the substrate by oxygen flushing the substrate (15 of FIG. 3), for example, the silicon substrate with oxidizing gas. The dangling bond can be combined with oxygen, that is, oxygen can be bonded to the substrate at any available sites, not only by performing the oxygen flushing, but also by performing ozone cleaning and forming a silicon oxide film. Also, the oxygen flushing may not be performed on the substrate 15.

After loading the substrate 15 into the reaction chamber (11 of FIG. 3), the processing temperature of the reaction chamber 11 is maintained to be between 100 and 400°C, preferably between 300 and 350°C, and the processing pressure of the reaction chamber 11 is maintained to be between 1 and 10,000 mTorr, using a heater (not shown) (step 23). The processing temperature and the processing pressure are maintained in the successive steps, however, they can be changed, if necessary.

The first reactant such as trimethyl aluminum ( $\text{Al}(\text{CH}_3)_3$ : TMA) is injected into the reaction chamber 11 through the gas inlet A and the shower head 17 for a long enough time to

cover the surface of the substrate, for example, between 1 msecond and 10 seconds, by opening the first valve V1, while the processing temperature and the processing pressure are maintained (step 25). By doing so, the first reactant is chemisorbed into the oxygen flushed silicon substrate.

The reaction chamber 11 is purged with inert gas such as argon for between 0.1 and 100 seconds by selectively opening the second valve V2 while the processing temperature and the processing pressure are maintained (step 27). By doing so, the first reactant which is only physically deposited on the substrate 15 is removed.

The second reactant, for example, oxidizing gas which does not contain a hydroxide is injected into the reaction chamber 11 through the shower head 17 by opening the third valve (V3) while the processing temperature and the processing pressure are maintained (step 29).  $N_2O$ ,  $O_2$ ,  $O_3$ , or  $CO_2$  gas can be used as the second reactant. By doing so, the chemisorbed first reactant reacts with the second reactant. Accordingly, the first reactant is chemically exchanged to form a metal-oxygen atomic layer film. The second reactant does not fully react with the first reactant. However, it is possible to form the metal-oxygen atomic layer without generating a hydroxide in a metal oxide film as described later on.

Unnecessary reactants are removed by purging the reaction chamber 11 with inert gas a second time for between 0.1 and 100 seconds while the processing temperature and the processing pressure are maintained (step 31).

The third reactant, for example, an oxide such as water vapor is injected into the reaction chamber 11 through the shower head 17 for a long enough time to cover the surface of the substrate, for example, between 1 msecond and 10 seconds, by opening a fourth valve V4 (step 33). By doing so, since the third reactant more actively reacts with the first reactant than the second reactant does, the first reactant which did not react with the second reactant, reacts with the third reactant and is chemically exchanged to further contribute to the formation of the metal-oxygen atomic layer film. At this time, since the available amount of the first reactant is reduced by previously reacting the second reactant, which does not contain a hydroxide, with the first reactant, a metal oxide film in units of atomic layers in which the generation of a hydroxide is prevented is formed.

In the present embodiment, an aluminum oxide film ( $Al_2O_3$ ) is an example of the metal oxide film. However, a  $TiO_2$  film, a  $ZrO_2$  film, a  $HfO_2$  film, a  $Ta_2O_5$  film, a  $Nb_2O_5$  film, a  $CeO_2$  film, a  $Y_2O_3$  film, a  $SiO_2$  film, a  $In_2O_3$  film, a  $RuO_2$  film, a  $IrO_2$  film, a  $SrTiO_3$

film, a  $\text{PbTiO}_3$  film, a  $\text{SrRuO}_3$  film, a  $\text{CaRuO}_3$  film, a  $(\text{Ba,Sr})\text{TiO}_3$  film, a  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  film, a  $(\text{Pb,Lu})(\text{Zr,Ti})\text{O}_3$  film, a  $(\text{Sr,Ca})\text{RuO}_3$  film, a  $(\text{Ba,Sr})\text{RuO}_3$  film, a  $\text{In}_2\text{O}_3(\text{ITO})$  film doped with Sn, and a  $\text{I}_2\text{O}_3$  film doped with Zr are other examples of metal oxide films which can be created according to the present invention.

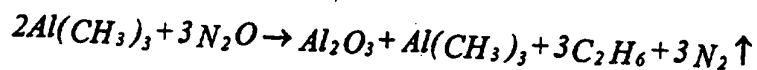
One cycle in which the metal oxide film in units of atomic layers is formed by removing the unnecessary reactants by purging the reaction chamber 11 with inert gas for between 0.1 seconds and 100 seconds while the processing temperature and pressure are maintained, is completed (step 35). It is possible to prevent the third reactant from reacting with the first reactant to the highest degree by further performing a step of injecting and purging the second reactant which does not contain a hydroxide after purging the reaction chamber the third time.

Then, it is checked whether the thickness of the metal oxide film formed on the substrate is appropriate, for example, between 10 Å and 1,000 Å (step 37). When the thickness of the metal oxide film is appropriate, the step of forming the metal oxide film is completed. When the metal oxide film is not thick enough, the steps from the step of injecting the first reactant into the reaction chamber to the step of purging the reaction chamber a third time (step 35) are cyclically repeated.

FIGS. 23A through 23D illustrate the combination relationship between reactants adsorbed on a substrate when an the aluminum oxide film is formed by a method of forming a thin film using an ALD method according to a second embodiment of the present invention. The substrate 15, for example, the silicon substrate, is oxygen flushed, thus combining the dangling bond of the substrate 15 with oxygen, as shown in FIG. 23A. That is, therefore, at any sites where oxygen can be bonded to the substrate 15, oxygen is bonded to the surface of the substrate as shown in FIG. 23A. The substrate 15 may not be oxygen flushed, if it is not necessary.

After injecting trimethyl aluminum ( $\text{Al}(\text{CH}_3)_3$ ) which is the first reactant into the reaction chamber whose processing temperature is maintained to be between 100 and 400°C and whose processing pressure is maintained to be between 1 and 10,000 mTorr, the reaction chamber is purged with argon gas. By doing so, only the first reactant which is chemisorbed into the oxygen flushed substrate remains as shown in FIG. 6. Namely, various forms of bonds such as Si-O, Si-O- $\text{CH}_3$ , and Si-O-Al- $\text{CH}_3$  are formed on the silicon substrate.

The second reactant which does not include a hydroxide such as  $N_2O$ ,  $O_2$ ,  $O_3$ , or  $CO_2$  is injected into the reaction chamber 11. For example, when  $N_2O$  is used as the second



reactant, the reaction proceeds as follows.

As shown in the chemical formula 1, when  $N_2O$  which does not contain a hydroxide is injected into trimethyl aluminum, trimethyl aluminum is consumed and  $Al_2O_3$  is formed. That is to say, the chemisorbed first reactant reacts with the second reactant. Accordingly, the first reactant is chemically exchanged to further contribute to the formation of the metal-oxygen atomic layer film as shown in FIG. 23C. Namely, bonds of the form Si-O-Al-O are formed on the silicon substrate.

After injecting the third reactant, such as water vapor, into the reaction chamber, the reaction chamber is purged with argon gas. By doing so, the first reactant which did not react with the second reactant, reacts with the third reactant and is changed to form the metal-oxygen atomic layer as shown in FIG. 23D. At this time, the metal-oxide film in units of atomic layers, in which generation of hydroxide is inhibited, is formed since the available amount of the first reactant is reduced by previously reacting the second reactant, which does not include a hydroxide, with the first reactant.

The way in which the aluminum oxide film in units of atomic layers, in which the absolute amount of a hydroxide is small, is formed will now be described in detail.

The inventors discovered that the undesired by-product  $Al(OH)_3$  is contained in the aluminum oxide film by the reaction represented by chemical formula 2, when the aluminum oxide film is formed by a conventional ALD method. In order to look for the by-product  $Al(OH)_3$ , the present inventors performed an x-ray photoelectron spectroscopy (XPS) analysis of the aluminum oxide film formed by the conventional ALD method.

FIG. 24 is an x-ray photoelectron spectroscopy (XPS) graph of an aluminum oxide film formed by the conventional ALD method. In FIG. 24, the X axis denotes binding energy and the Y axis denotes the electron count in arbitrary units.

It is noted that the right side of the curve b is a little wider than the right side of the curve a when the curves overlap each other centering around 535.1eV in the aluminum oxide film peak formed by the conventional ALD method. That is to say, the aluminum oxide film formed by the conventional ALD method shows a graph (b) having a width wider than a

graph (a) of a pure aluminum oxide film since  $\text{Al}(\text{OH})_3$  is contained in the film formed by the conventional method.

Considering the above, when trimethyl aluminum directly reacts with water vapor like in the conventional technology, a large amount of  $\text{Al}(\text{OH})_3$ , which contains a hydroxide, is created by the reaction represented by chemical formula 2. Therefore, in order to reduce the amount of  $\text{Al}(\text{OH})_3$ , the absolute amount of the trimethyl aluminum which reacts with water vapor must be reduced. In the present invention, since the absolute amount of trimethyl aluminum is reduced by reacting trimethyl aluminum with  $\text{N}_2\text{O}$ , which does not contain hydroxide, and then reacting the remaining un-reacted trimethyl aluminum with water vapor, the aluminum oxide film in units of atomic layers is formed with a small absolute amount of a hydroxide.

FIGS. 25A and 25B are graphs showing the leakage current characteristics of aluminum oxide films manufactured by the conventional method and the second embodiment of the present invention, respectively. The leakage current characteristics are investigated by applying the aluminum oxide film to a capacitor. A polysilicon film is used as the lower electrode and as the upper electrode of the capacitor. In FIGS. 25A and 25B, first curves a and c denote results of measuring the amount of current for a cell, which flows through a dielectric film, when the lower electrode is connected to ground and a voltage between 0 and 5 V is applied to the upper electrode. Second curves b and d denote results of measuring the amount of current for a cell, which flows through the dielectric film, under the same conditions that the first measurement was performed under, after the first measurement. As shown in FIG. 25B, when the aluminum oxide film formed by the present invention is used as the dielectric film, the leakage current is smaller at a given voltage, for example, 2 V, compared with the conventional case of FIG. 25A at the same voltage and the distance between the first curve and the second curve is short. Accordingly, it is noted that leakage current characteristics are improved by the present invention.

### Third Embodiment

FIG. 26 is a flowchart for a method of forming a thin film using an ALD method according to a third embodiment of the present invention. FIG. 27 is a timing diagram showing the supply of reactants during the formation of the thin film using the ALD method

according to the third embodiment of the present invention. In the following description, the formation of an aluminum oxide film is taken as an example.

The dangling bond of the substrate, which may be a silicon substrate, is terminated by oxygen or nitrogen flushing the substrate 15 using oxidizing or nitriding gas (step 41). That is, at any sites where oxygen can be bonded to the substrate which may be a silicon substrate, oxygen is bonded to the substrate by oxygen or nitrogen flushing the substrate 15 using oxidizing or nitriding gas. The oxygen or nitrogen flushing can be performed using not only the atomic layer thin film forming apparatus shown in FIG. 3, but also other apparatuses. Moreover, the dangling bond can be combined with oxygen or nitrogen, that is, at any sites where oxygen or nitrogen can be bonded to the substrate, oxygen or nitrogen is bonded to the substrate, not only by performing the oxygen or nitrogen flushing but also by performing ozone cleaning and forming a silicon oxide film and a silicon nitride film. The oxygen or nitrogen flushing may not be necessary.

After loading the substrate 15 into the reaction chamber 11, the processing temperature of the reaction chamber 11 is maintained to be between 100 and 400°C, preferably between 300 and 350°C, and the processing temperature of the reaction chamber 11 is maintained to be between 1 and 10,000 mTorr using a heater (not shown) and a pump 19 (step 43). The processing conditions are maintained in the successive steps, however, they can be changed, if necessary.

A first reactant, such as trimethyl aluminum ( $\text{Al}(\text{CH}_3)_3$ : TMA), is injected into the reaction chamber 11 through the gas inlet A and the shower head 17 for a long enough time to cover the surface of the substrate, for example, between 1 msecond and 10 seconds by opening the first valve V1, while the processing conditions are maintained (step 45). By doing so, the first reactant is chemisorbed into the oxygen or nitrogen flushed silicon substrate.

The reaction chamber 11 is purged a first time by an inert gas such as argon gas for between 0.1 and 100 seconds by selectively opening the second valve V2, while the processing conditions are maintained (step 47). By doing so, any first reactant which is only physically deposited on the substrate 15 is removed.

A second reactant, for example, oxidizing gas which has excellent oxidizing power, like water vapor is injected into the reaction chamber 11 through the shower head 17 by opening the third valve (V3), while the processing conditions are maintained (step 49).

In doing so, the chemisorbed first reactant reacts with the second reactant forming a thin film in units of atomic layers, that is, an aluminum oxide film is formed by chemical exchange. Namely,  $\text{CH}_3$  of TMA reacts with H of  $\text{H}_2\text{O}$ , thus forming  $\text{CH}_4$ , which is removed. Al of TMA reacts with O of  $\text{H}_2\text{O}$ , thus forming  $\text{Al}_2\text{O}_3$ . Since the atomic layer thin film is formed at a temperature of  $400^\circ\text{C}$  or less, which is low, TMA is not completely decomposed. Accordingly, a large amount of impurities such as carbon or OH form bonds in the aluminum oxide film.

Any second reactant which did not react with the first reactant and is only physisorbed into the substrate 15 is removed by purging the reaction chamber 11 a second time with inert gas such as argon gas for between 0.1 and 100 seconds, while the processing conditions are maintained (step 51).

A third reactant for removing impurities and improving the stoichiometry of the thin film, for example, an oxidizing gas such as ozone is injected into the reaction chamber through a fourth valve V4 and the shower head for a long enough time to cover the surface of the substrate on which the thin film is formed, for example, between 1msecond and 10 seconds (step 53). By doing so, it is possible to remove impurities such as carbon or OH which is bonded to and contained in the thin film in units of atomic layers, and to solve the problem that there is a lack of oxygen in the aluminum oxide film. Accordingly, it is possible to obtain a thin film with excellent stoichiometry.

A cycle during which the thin film in units of atomic layers is formed, is completed by purging the reaction chamber 11 a third time with an inert gas for between 0.1 and 100 seconds while the processing conditions are maintained, thus removing the un-reacted physisorbed third reactant (step 55).

It is checked whether the thickness of the thin film in units of atomic layers formed on the substrate is appropriate, for example, between 10 Å and 1,000 Å (step 57). When the thickness of the thin film is appropriate, the process of forming the thin film is completed. When the thin film is not thick enough, the steps, from the step (step 45) of injecting the first reactant to the step (step 55) of purging the reaction chamber a third time, are cyclically repeated.

In the present embodiment, the aluminum oxide film is formed using trimethyl aluminum ( $\text{Al}(\text{CH}_3)_3$ : TMA) as the first reactant, water vapor which is oxide gas as the second reactant, and ozone gas for removing the impurities as the third reactant. However, it

is possible to form a titanium nitride film using  $\text{TiCl}_4$  as the first reactant,  $\text{NH}_3$  as the second reactant, and nitrogen gas for removing impurities and improving the stoichiometry of the thin film as the third reactant.

Furthermore, according to the method of forming an atomic layer thin film of the present invention, it is possible to form a single atomic oxide, a composite oxide, a single atomic nitride, or a composite nitride other than an aluminum oxide film or a titanium nitride film.  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{RuO}_2$ , and  $\text{IrO}_2$  are examples of single atomic oxides.  $\text{SrTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrRuO}_3$ ,  $\text{CaRuO}_3$ ,  $(\text{Ba},\text{Sr})\text{TiO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Sr},\text{Ca})\text{RuO}_3$ ,  $\text{In}_2\text{O}_3$  doped with Sn,  $\text{In}_2\text{O}_3$  doped with Fe, and  $\text{In}_2\text{O}_3$  doped with Zr are examples of composite oxides.  $\text{SiN}$ ,  $\text{NbN}$ ,  $\text{ZrN}$ ,  $\text{TiN}$ ,  $\text{TaN}$ ,  $\text{Y}_3\text{N}_5$ ,  $\text{AlN}$ ,  $\text{GaN}$ ,  $\text{WN}$ , and  $\text{BN}$  are examples of single atomic nitrides.  $\text{WBN}$ ,  $\text{WSiN}$ ,  $\text{TiSiN}$ ,  $\text{TaSiN}$ ,  $\text{AlSiN}$ , and  $\text{AlTiN}$  are examples of composite nitrides.

A thin film formed by the method of forming a thin film using the ALD method according to the present invention can be applied to semiconductor devices. For example, the thin film can be used as a gate oxide layer, the electrode of a capacitor, an etching stopping film, a capping film for preventing reaction, an anti-reflection film during a photolithography process, a barrier metal film, a selective deposition film, or a metal gate electrode.

FIG. 28 is a graph showing the thickness of an aluminum oxide film manufactured by the method of forming an atomic layer thin film according to the third embodiment of the present invention as a function of the number of times the steps of the method are repeated cycles. One cycle includes the steps of injecting the first reactant into the reaction chamber, purging the reaction chamber of the physisorbed first reactant, injecting the second reactant into the reaction chamber, purging the reaction chamber of the physisorbed second reactant, injecting the third reactant into the reaction chamber, and purging the reaction chamber of the physisorbed third reactant. As shown in FIG. 28, according to the thin film manufacturing method of the present invention, since the aluminum oxide film is grown to a thickness of 1.1 Å each cycle and the thickness of the aluminum oxide film linearly increases in proportion to the number of cycles, the aluminum oxide film is easily formed by the atomic layer deposition method of the present invention.

FIG. 29 is a graph illustrating the uniformity of an aluminum oxide film manufactured by the method of forming an atomic layer thin film according to the third embodiment of the present invention. The X axis denotes the positions of nine points: the central point of an



eight-inch substrate, four points separated by  $90^\circ$  on the circumference of a circle having a diameter of 1.75 inches, and another four points spaced apart by  $90^\circ$  on the circumference of a circle having a diameter of 3.5 inches. The Y axis denotes the thickness of the aluminum oxide film. As shown in FIG. 29, the uniformity of the aluminum oxide film is excellent over the eight-inch substrate.

FIGS. 30A and 30B are graphs for analyzing the aluminum peaks of aluminum oxide films manufactured by the conventional technology and the method of forming an atomic layer thin film according to the third embodiment of the present invention, respectively, using XPS. To be specific, the X axis denotes binding energy and the Y axis denotes the electron count. In the conventional aluminum oxide film, a large amount of Al-Al bonding occurs as shown in FIG. 30A. In the aluminum oxide film according to the present invention, almost no Al-Al bonding occurs and Al-O bonding is most prominent, as shown in FIG. 30B. Accordingly, it is noted that the stoichiometry of the aluminum oxide film according to the present invention is excellent.

FIGS. 31A and 31B are graphs for analyzing the carbon peaks of aluminum oxide films manufactured by the conventional technology and the method of forming a thin film using the ALD method according to the third embodiment of the present invention, respectively, using XPS. To be specific, the X axis denotes the binding energy and the Y axis denotes electron count. In the conventional aluminum oxide film, a carbon peak is shown, as in FIG. 31A, which means that a large amount of carbon is contained in the aluminum oxide film. In the aluminum oxide film according to the present invention, no carbon peak is shown in FIG. 31B. Therefore, it is possible to obtain an aluminum oxide film in which impurities such as carbon are reduced according to the present invention.

#### Fourth Embodiment

FIG. 32 is a flowchart for a method of forming an atomic layer thin film according to a fourth embodiment of the present invention. In FIG. 32, the reference numerals identical to those of FIG. 22 denote identical steps.

The fourth embodiment of the present invention is a combination of the second embodiment and the third embodiment. Specifically, the fourth embodiment is the same as the second and third embodiments except that the reaction chamber is purged a fourth time (step 36b) after injecting a fourth reactant, for example, an oxidizing gas such as ozone gas for removing impurities and improving the stoichiometry of the thin film, into the reaction chamber through the third valve V3 and the shower head 17 for a long enough time to cover the surface of the substrate on which the thin film is formed, for example, between 1 msecond and 10 seconds, like in the third embodiment (step 36a), after purging the reaction chamber a third time in the second embodiment.

By doing so, it is possible to remove impurities such as bonded carbon or OH bond, which are contained in the metal oxide film in units of atomic layers, and to solve the problem that oxygen is lacking in the metal oxide film, to thus obtain a highly pure thin film. That is to say, according to the present invention, it is possible to obtain a thin film of desired quality and to minimize the density of the impurities by increasing the probability that the main reactants react with each other before or after injecting them. Thus, impurities of the thin film other than the main reactants may be removed and the

quality of the thin film may be improved through a complete reaction, in forming a thin film by an atomic layer deposition (ALD) method according to the present invention.

As mentioned above, in the method of forming a thin film using an ALD method according to an embodiment of the present invention, the ligand of the first reactant A is separated due to a difference in binding energy, without the movement of a radical from the second reactant B to the first reactant A. A volatile vapor phase material is formed by the combination of ligands and the vapor phase material is removed by purging. As a result, according to the method of forming a thin film using an ALD method of the present invention, it is possible to reduce the impurities generated in a thin film by sub-reactions, since the movement of the radical does not occur.

In the method of forming a thin metal oxide film using an ALD method according to another embodiment of the present invention, it is possible to prevent the generation of by-products such as hydroxide in the metal oxide film by reducing the absolute amount of the first reactant by previously reacting the first reactant with a second reactant which does not contain hydroxide, and then reacting the first reactant with a third reactant which contains a hydroxide. For example, it is possible to form an aluminum oxide film in which the absolute amount of hydroxide is small by reducing the absolute amount of trimethyl aluminum by previously reacting trimethyl aluminum with  $N_2O$  which does not contain a hydroxide, and then reacting trimethyl aluminum with water vapor.

Also, in the method of forming a thin film using an ALD method according to another embodiment of the present invention, a third reactant for removing the impurities and improving the stoichiometry of the thin film is injected into the reaction chamber and the reaction chamber is purged of the third reactant, when the atomic layer deposition method is used. By doing so, it is possible to obtain a thin film with excellent stoichiometry which does not contain impurities.

## CLAIMS:

1. A method of forming a thin film using an atomic layer deposition (ALD) method, the method comprising the steps of:
  - injecting a first reactant including an atom that forms the thin film and a ligand into a reaction chamber that comprises a substrate so that the first reactant is chemisorbed into the substrate;
  - removing any first reactant which is only physisorbed into the substrate by purging the reaction chamber with inert gas; and
  - forming a thin film in units of atomic layers by a chemical reaction between the atom that forms the thin film and a second reactant whose binding energy with respect to the atom that forms the thin film is larger than the binding energy of the ligand with respect to the atom that forms the thin film by injecting the second reactant into the reaction chamber and removing the ligand without generating by-products.
2. The method of claim 1, wherein the first reactant is  $\text{Al}(\text{CH}_3)_3$  and the second reactant is an activated oxidizing agent.
3. The method of claim 2, wherein the activated oxidizing agent is selected from the group consisting of  $\text{O}_3$ ,  $\text{O}_2$  plasma, and  $\text{N}_2\text{O}$  plasma.
4. The method of claim 1, further comprising the step of removing any physisorbed second reactant by purging the chamber with inert gas after the step of injecting the second reactant.
5. The method of claim 4, wherein the steps, from the step of injecting the first reactant to the step of removing any physisorbed second reactant, are repeated a plurality of times as necessary.
6. A method of forming a thin film using an ALD method, comprising the steps of:

injecting a first reactant into a reaction chamber that comprises a substrate, so that the first reactant is chemically adsorbed into the substrate;

removing any first reactant which is only physisorbed into the substrate by purging the reaction chamber with inert gas;

chemically exchanging the chemisorbed first reactant to form a metal-oxygen atomic layer film by injecting a second reactant which does not contain a hydroxide into the reaction chamber;

removing any physisorbed second reactant by purging the reaction chamber with inert gas; and

forming a metal oxide film in units of atomic layers while the generation of a hydroxide is prevented by injecting a third reactant into the reaction chamber, thus chemically exchanging the remaining chemisorbed first reactant to further contribute to the formation of the metal-oxygen atomic layer.

7. The method of claim 6, wherein the first reactant is a metal reactant, the second reactant which does not contain a hydroxide is  $N_2O$ ,  $O_2$ ,  $O_3$ , or  $CO_2$ , and the third reactant is oxidizing gas.

8. The method of claim 6, wherein the temperature of the reaction chamber is maintained to be between 100 and 400°C from the step of injecting the first reactant to the step of injecting the third reactant.

9. The method of claim 6, wherein the metal oxide film is one selected from the group consisting of a  $Al_2O_3$  film, a  $TiO_2$  film, a  $ZrO_2$  film, a  $HfO_2$  film, a  $Ta_2O_5$  film, a  $Nb_2O_5$  film, a  $CeO_2$  film, a  $Y_2O_3$  film, a  $SiO_2$  film, a  $In_2O_3$  film, a  $RuO_2$  film, a  $IrO_2$  film, a  $SrTiO_3$  film, a  $PbTiO_3$  film, a  $SrRuO_3$  film, a  $CaRuO_3$  film, a  $(Ba,Sr)TiO_3$  film, a  $Pb(Zr,Ti)O_3$  film, a  $(Pb,La)(Zr,Ti)O_3$  film, a  $(Sr,Ca)RuO_3$  film, a  $(Ba,Sr)RuO_3$  film, a  $In_2O_3(ITO)$  film doped with Sn, and a  $I_2O_3$  film doped with Zr.

10. The method of claim 6, wherein the dangling bond of the surface of the substrate is terminated by injecting oxidizing gas before injecting the first reactant, when the substrate is a silicon substrate.

11. The method of claim 6, further comprising the step of removing any physisorbed third reactant by purging the reaction chamber with inert gas after the step of injecting the third reactant into the reaction chamber.
12. The method of claim 11, wherein the steps, from the step of injecting the first reactant to the step of removing any physisorbed third reactant, are repeated a plurality of times as necessary.
13. The method of claim 11, further comprising the step of injecting a fourth reactant for removing impurities and improving the stoichiometry of the metal oxide film into the reaction chamber after the step of removing the physisorbed third reactant.
14. The method of claim 13, wherein the fourth reactant is ozone gas.
15. A method of forming a thin film using an ALD method, comprising the steps of:
- injecting a first reactant into a reaction chamber into which a substrate is loaded so that the first reactant is chemically adsorbed into the substrate;
  - removing any first reactant which is only physisorbed into the substrate by purging the reaction chamber with inert gas;
  - forming a thin film in units of atomic layers by injecting a second reactant into the reaction chamber and chemically exchanging the first reactant to further contribute to the formation of the second reactant;
  - removing any physisorbed second reactant by purging the reaction chamber with inert gas; and
  - injecting a third reactant for removing impurities and improving the stoichiometry of the thin film into the reaction chamber in which the thin film is formed.
16. The method of claim 15, wherein the first reactant is a metal reactant and the second and third reactants are oxidizing gases.

17. The method of claim 15, wherein the thin film is a metal oxide film formed of a single atomic oxide or a composite oxide.
18. The method of claim 17, wherein the single atomic oxide is one selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{RuO}_2$ , and  $\text{IrO}_2$ .
19. The method of claim 17, wherein the composite oxide is one selected from the group consisting of  $\text{SrTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrRuO}_3$ ,  $\text{CaRuO}_3$ ,  $(\text{Ba},\text{Sr})\text{TiO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Sr},\text{Ca})\text{RuO}_3$ ,  $\text{In}_2\text{O}_3$  doped with Sn,  $\text{In}_2\text{O}_3$  doped with Fe, and  $\text{In}_2\text{O}_3$  doped with Zr.
20. The method of claim 15, wherein the first reactant is a metal reactant and the second and third reactants are nitriding gases.
21. The method of claim 15, wherein the thin film is a metal nitride film formed of a single atomic nitride or a composite nitride.
22. The method of claim 21, wherein the single atomic nitride is one selected from the group consisting of  $\text{SiN}$ ,  $\text{NbN}$ ,  $\text{ZrN}$ ,  $\text{TiN}$ ,  $\text{TaN}$ ,  $\text{Y}_3\text{N}_5$ ,  $\text{AlN}$ ,  $\text{GaN}$ ,  $\text{WN}$ , and  $\text{BN}$ .
23. The method of claim 21, wherein the composite nitride is one selected from the group consisting of  $\text{WBN}$ ,  $\text{WSiN}$ ,  $\text{TiSiN}$ ,  $\text{TaSiN}$ ,  $\text{AlSiN}$ , and  $\text{AlTiN}$ .
24. The method of claim 15, further comprising the step of removing any physisorbed third reactant by purging the reaction chamber with inert gas after the step of injecting the third reactant.
25. The method of claim 15, the dangling bond of the surface of the substrate is terminated by injecting oxidizing gas or nitriding gas before injecting the first reactant, when the substrate is a silicon substrate.

26. The method of claim 15, wherein the temperature of the reaction chamber is maintained to be between 100 and 400°C from the step of injecting the first reactant to the step of injecting the third reactant.

27. The method of claim 15, further comprising the step of removing any physisorbed third reactant by purging the reaction chamber with inert gas after the step of injecting the third reactant.

28. The method of claim 27, wherein the steps, from the step of injecting the first reactant to the step of removing the physisorbed third reactant, are repeated a plurality of times as necessary.





Application No: GB 0024571.2  
 Claims searched: 1-5

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Examiner: Pete Beddoe  
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## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): C7F (FHB, FHE, FHX, FCXE, FCXL, FCXM, FCXX, FCVE, FCVL, FCVM, FCVX)

Int Cl (Ed.7): C23C (14/00, 14/08, 16/44); C30B (23/02, 23/08, 25/00, 25/02); H01L 21/316

Other: Online: WPI, EPODOC, JAPIO

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X,P	GB 2340508 A (SAMSUNG) 23 February 2000 see esp col6 line 16 - col9 line 13	1 at least
X	GB 2162862 A (RESEARCH DEVELOPMENT) see esp	1 at least
X,P	US 6090442 (UNIVERSITY TECHNOLOGY) 18 July 2000 see esp cols 5-8 & claim 1	1,2 at least
X	US 5374570 (FUJITSU) see esp col6 lines 3-12 & eg col8 lines 29-47	1-3 at least
X	US 4058430 (TUOMO) see esp exs	1.1 at least
X,P	JP 11-269652 A (SAMSUNG) & WPI Accession no 99-615894 see esp English abstract	1 at least
X	JP 1-204434 A (NEC) & WPI Accession no 89-281185 see esp English abstract	1-3 at least
X	JP 1-179423 A (NEC) & WPI Accession no 89-245666 see esp English abstract	1-3 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



Application No: GB 0024571.2  
Claims searched: 1-5

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Date of search: 23 February 2001

Category	Identity of document and relevant passage	Relevant to claims
X	Applied Physics Letters Vol. 51, No. 15, 12 October 1987, G-I Oya et al, "Growth of $\alpha$ -Al <sub>2</sub> O <sub>3</sub> films by molecular layer epitaxy", pages 1143-1145, esp p1143 line 36 (LHS) - line 14 (RHS)	1-3 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.